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I. *On the δ-Rays produced by α-Particles in Different Gases.*

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[Plates I. & II.]

§ 1. WHEN a metal plate is struck by α-particles an electronic radiation is emitted, which is often called the δ-radiation. It has been shown by Wertenstein †, Bumstead ‡, and others, using polonium as the source of α-particles, that δ-rays of low velocity, corresponding to a potential drop of a few volts, largely predominate, but that rays of all velocities up to about $2{\cdot}7 \times 10^9$ cm./sec. (2000 volts) are present. The number of δ-rays decreases rapidly as the velocity increases. These experiments have also shown that there is a close parallel between the production of δ-rays and the ionization produced by the α-particle ; the number of δ-rays varies with the range of the α-particle in much the same manner as the number of ions produced in a gas.

Further, by photographing the tracks of α-particles in hydrogen at a low pressure in a Wilson expansion apparatus, Bumstead obtained definite evidence of electron

* Communicated by the Authors.

† Wertenstein, *Le Radium*, ix. p. 6 (1912).

‡ Bumstead, Phil. Mag. xxii. p. 907 (1911), xxvi. p. 233 (1913); Bumstead & McGougan, Phil. Mag. xxiv. p. 462 (1912).

trails radiating from the main α-particle track *. Only a few exceptional electrons had sufficient velocity to emerge distinctly, but there appeared to be large numbers of δ-rays with small velocities, which formed knobs and projections on the track, giving it a ragged edge.

The track photographs which he obtained were too few and too indefinite to give any quantitative information. On the other hand, the electrical experiments gave a great deal of information concerning the velocity distribution of the δ-rays. He did not suggest any definite theory of their origin, but proposed an empirical formula to represent the observed distribution of velocities. His observations, however, are not in disagreement with a simple theory of the production of δ-rays, in which they are regarded as due to the collisions of the α-particle with the electrons in the matter through which it passes. On this view, the maximum velocity of a δ-ray is twice that of the α-particle at the moment of impact, and such a δ-ray is produced in the very rare event of a head-on collision. The more frequent collisions give rise to δ-rays of low velocity, so that the number of δ-rays increases rapidly as their velocity decreases. This theory explains in a general way the results obtained by Bumstead, but the conditions of his experiments were not sufficiently definite to provide a suitable test.

More recently C. T. R. Wilson has published some photographs of α-ray tracks in air †, showing the presence of δ-rays. He estimated that the δ-ray of maximum range had a velocity about twice that of the α-particle ; it appeared, however, to be ejected nearly at right angles to the direction of motion of the α-particle, and not along the direction of motion, as the simple collision theory would require. He suggested that there might be some connexion between the emission of the δ-rays and the fact that the velocity of the α-particle was about the same as the velocities of the electrons in the K-orbits of nitrogen and oxygen.

In the present experiments we have investigated the production of δ-rays by photographing the tracks of α-particles in a Wilson cloud chamber We have directed our attention to the following points :—

(1) The energy and direction of emission of the δ-rays.
(2) The dependence of the production of δ-rays on the velocity of the α-particle.
(3) The dependence of the production of δ-rays on the gas through which the α-particle passes.

* Bumstead, Phys. Rev. viii. p. 715 (1916).
† C. T. R. Wilson, Proc. Camb. Phil. Soc. xxi. p. 405 (1922).

The photographs have not been analysed in great detail, but, as far as our results go, we find that the simple collision theory gives a satisfactory picture of the production of δ-rays.

§ 2. The cloud chamber was of the large type described by Wilson *, consisting essentially of a thin brass piston moving in a brass cylinder with a glass top. The internal diameter of the glass cylindrical top was about 18 cm. and the depth 4 cm. The general method of working with an expansion chamber is so well known that no details need be given. In general, Wilson's procedure was closely followed, though some mechanical details were changed. The expansion was produced by opening a valve and so connecting the interior of the piston to a large evacuated bulb. After a suitable interval of time a battery of Leyden jars was discharged through a mercury-vapour lamp, which sent a horizontal parallel beam of light through the cloud chamber. The mechanism for opening the valve and completing the lighting circuit consisted of two heavy compound pendulums joined by a wire. They were released simultaneously: one opened the valve and produced the expansion, the other completed the lighting circuit and illuminated the tracks. The periods of the pendulums could be changed by adjusting the position of sliding weights, and the time-interval between the two events was chosen so as to give the sharpest tracks.

The tracks were photographed through the plate-glass top of the expansion chamber, by a camera vertically above. The camera was stereoscopic, the maximum apertures of the lenses being $f/4{\cdot}5$.

Gases were introduced into the cloud chamber through a small capillary tap fitting into the curved glass side. The cloud chamber could also be connected to a manometer, on which the initial and final pressures of the gas in the chamber could be measured. In most experiments the initial pressure was atmospheric, but in some cases the pressure was reduced to about 15 cm. of mercury. The tracks were examined in four gases—air, argon, helium, and hydrogen.

Air was admitted directly from the room.

The argon was prepared from commercial argon, containing about 20 per cent. of nitrogen, by passing the gas over a heated mixture of lime and magnesium powder.

The helium was initially mixed with about 20 per cent. of

* C. T. R. Wilson, Proc. Roy. Soc. A, lxxxvii. p. 277 (1912).

air. It was purified by passage over charcoal cooled in liquid air.

Commercial electrolytic hydrogen was used. This was found to be preferable to that generated in a Kipp apparatus from zinc and hydrochloric acid, which even after bubbling through water frequently gave a slight general fog on expansion, perhaps due to traces of hydrocarbons.

The source of α-particles was the active deposit of thorium, obtained on the end of a brass rod of 2 mm. diameter, by exposure to thorium emanation. The source could be placed either inside or outside the expansion chamber. In the latter case the α-particles entered the chamber through a mica window of known stopping power. The source, Th(B + C), gave two sets of α-particles, of ranges 4·8 cm. and 8·6 cm., corresponding to initial velocities of $1{\cdot}70 \times 10^9$ cm./sec. and $2{\cdot}06 \times 10^9$ cm./sec.

§ 3. A large number of α-ray tracks was photographed. Some typical tracks, illustrating the various points in connexion with the production of δ-rays, are shown in the accompanying plates (Pls. I. and II.): the magnification is expressed relative to the length of track in the specified gas at atmospheric pressure, and the direction of motion of the α-particle is from left to right.

It will be seen from these photographs that the δ-ray tracks are exactly similar to those of slow electrons which have been described by C. T. R. Wilson, and show the characteristic curly ends accompanied by intense ionization.

A careful examination of the satisfactory photographs has led us to the conclusion that all the phenomena can be explained on the assumption that the δ-rays are produced by collisions of the α-particles with the electrons of the atoms through which they pass, provided that account is taken of the fact that, in order that the δ-ray should be observed, sufficient energy must be communicated to it to take it clear of the main α-ray column. We shall now consider from this point of view the results obtained.

The photographs show at once that the δ-ray tracks are of varying length, and that the maximum length depends upon the gas in which the track is obtained. An examination of the early parts of the α-ray tracks showed that the δ-rays had a maximum length of 2 mm. in hydrogen, 2·6 mm. in helium, and about ·45 mm. in both air and argon, all at N.T.P. (Owing to slight disturbances in the neighbourhood of the α-ray source, the first centimetre of the track was seldom utilized, so that the maximum

δ-trail in the cases of air and argon was obtained for a somewhat smaller velocity of the α-particle than in the other cases.)

These numbers are in accord with the view that the δ-particles have a definite maximum velocity independent of the gas. Assuming that the relative stopping-power of an atom is the same for the δ-rays as for the α-particles, the ratios of the lengths of the δ-rays of maximum velocity should be:

$$\text{Air}-1 : \text{A}-1{\cdot}2 : \text{He}-5{\cdot}6 : \text{H}_2-4.$$

The observed ratios are:

$$\text{Air}-1 : \text{A}-1 : \text{He}-5{\cdot}8 : \text{H}_2-4{\cdot}4,$$

which are in sufficiently close agreement.

Further, on the view that the δ-rays are produced by collisions of α-particles with electrons of the atoms through which they pass, the maximum velocity of the δ-ray is equal to twice the velocity of the α-particle.

C. T. R. Wilson * has found that, for electrons of ranges in air between 2 mm. and 15 mm., the range is approximately proportional to the fourth power of the velocity. For such slow electrons as the δ-rays we might expect that the range would be more nearly proportional to the cube of the velocity, a relation which holds closely for α-particles of about the same velocities as the δ-rays. Assuming the cube law, we find that the velocity of the δ-ray of maximum range 0·45 mm. is about $3{\cdot}7 \times 10^9$ cm./sec. The velocity of the α-particle was about $1{\cdot}9$ to 2×10^9 cm./sec., so that the agreement is fairly good. A better agreement would be obtained by taking the range of the δ-ray to be proportional to the 3·5 power of the velocity, but for the purposes of this paper the cube relation is sufficiently close.

For all the gases examined the number of δ-rays per centimetre of the α-ray track remains roughly the same until about 3 cm. from the end of the α-track, when it falls off very rapidly. The number of δ-rays distinctly projecting from the initial portion of the α-track was about 10 per cm. for an initial pressure of one atmosphere, and was roughly the same in all cases. This latter observation is somewhat surprising at first sight, but it can be readily explained in a general way. The number of electrons present in a given volume at given temperature and pressure is proportional to the number of atoms in the molecule of the gas and to its

* C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).

atomic number. The probability of a collision between the α-particle and an electron in the gas, which will result in the electron receiving some specified momentum, is proportional to the number of electrons present, if the forces retaining them in the atom be neglected. Only such δ-rays as project from the main α-column will, however, be counted; and as the α-column is of about the same thickness in different gases, the minimum range of the δ-ray is also about the same in the different gases. The range of a δ-ray of given velocity is inversely proportional to the number of atoms in the molecule and, roughly, inversely proportional to the square root of the atomic weight. With increasing atomic weight of the gas the number of electrons set in motion by the α-particle per cm. path will increase, but the fraction of these recorded as δ-rays will diminish.

In the following calculation we shall assume that the collisions occur as if the electrons are free and initially at rest.

Let E, M, and V be the charge, mass, and velocity of the α-particle; e, m, and u the corresponding quantities for the electron after collision; and let θ be the angle between the direction of motion of the δ-ray and the initial line of motion of the α-particle.

If momentum and energy are conserved in the linear motion of these two particles, then

$$u = 2\mathrm{V}\cos\theta,$$

since m/M is negligibly small.

Thus the maximum velocity that can be imparted to the electron is twice that of the α-particle. For the large distances at which these collisions take place we may assume that the particles behave as point-charges, and that the law of force between them is that of the inverse square. It can then be shown that the number of electrons projected within an angle θ by a single α-particle in its passage through 1 cm. of gas is

$$n = \pi \mathrm{N}\mu^2 \tan^2\theta,$$

where N is the number of electrons per c.c. of the gas, and

$$\mu = \frac{\mathrm{E}e}{\mathrm{V}^2} \cdot \frac{1}{m},$$

m/M being again neglected.

In our experiments the swiftest α-particles had an initial range of 8·6 cm. in air at atmospheric pressure, corresponding to a velocity of $2{\cdot}06 \times 10^9$ cm./sec. Substituting this value

for V, we find $\mu = 12 \times 10^{-11}$, and if the particles pass through hydrogen at N.T.P.,

$$n = 2{\cdot}4 \times \tan^2 \theta.$$

Now we observe as δ-rays only those electrons which are given a certain minimum velocity such as to give a trail which projects from the α-ray track. The minimum range which can be identified as a δ-ray depends on the sharpness of the α-ray track. This varies somewhat in the different photographs, but on the average the minimum range for the δ-ray is about ·15 to ·2 mm. The δ-ray of maximum range in hydrogen had a length of 2 mm. This corresponds, therefore, to a velocity of 2V. Assuming that the range of the δ-ray is proportional to the cube of the velocity—a rule which holds for α-particles of similar velocities to the δ-rays,—we find that only those δ-rays are definitely recognizable in the photographs which are projected within an angle θ of the direction of motion of the α-particle, where θ is given by

$$\cos \theta = \sqrt[3]{\frac{\cdot 2}{2}} = \cdot 46.$$

Hence the number of δ-rays per cm. on the track of an α-particle of velocity $2{\cdot}06 \times 10^9$ cm./sec. through hydrogen gas should be

$$n = 2{\cdot}4 \tan^2 \theta = 2{\cdot}4 \ (\sec.^2 \theta - 1) = 9.$$

A similar calculation for an α-particle passing through air gives $n = 11{\cdot}5$, and in helium $n = 11$.

In the case of argon we must remember that the electrons in the K orbits cannot be regarded as free, even for the purposes of this rough calculation, for the ionization potential of the K level is over 3000 volts. The K electrons must therefore be omitted, for they will only be removed from the atom by a very close collision of the α-particle, and their final energy of collision will also be small. We find, then, that for argon n is about 12.

Thus to a first approximation the tracks of α-particles in the four gases used will show the same number of δ-rays per centimetre of the track. The δ-rays will of course be much more obvious in hydrogen and helium, on account of their greater range in these gases.

In a similar way we can explain why the number of δ-rays is approximately constant along the earlier portion of the α-ray track, and falls off very rapidly in the last 2 or 3 centimetres equivalent range in air. We shall take the case of

an α-track in hydrogen. The number of δ-rays projected within an angle θ by an α-particle of velocity V is

$$n = 2{\cdot}4 \tan^2\theta \cdot \left(\frac{V_0}{V}\right)^4,$$

where $V_0 = 2{\cdot}06 \times 10^9$ cm./sec.

The δ-ray, in order to be observed, must have a minimum range of ·2 mm. Since the velocity of a δ-ray of range 2 mm. in hydrogen is $2V_0$, and assuming that the range is proportional to the cube of the velocity, the δ-ray, if this is to have sufficient velocity to be observed, must be projected within an angle θ, given by

$$\cos\theta = {\cdot}46 \cdot \frac{V_0}{V}.$$

Writing

$$\tan^2\theta = \sec.^2\theta - 1 = 4{\cdot}6 \cdot \frac{V^2}{V_0^2} - 1,$$

we find that the number of δ-rays per cm. on the track of an α-particle of velocity V is

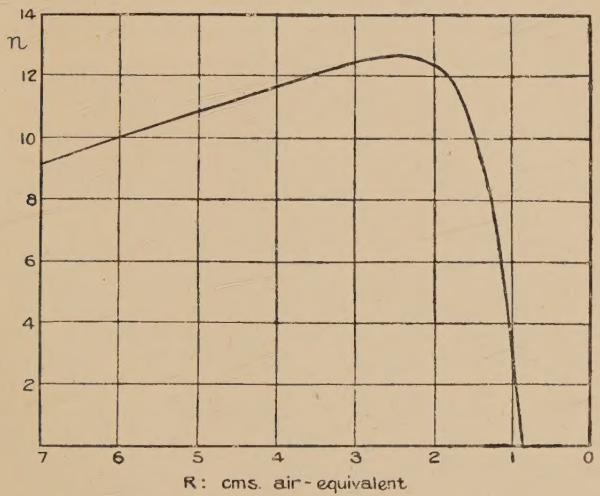
$$n = 2{\cdot}4 \frac{V_0^4}{V^4} \cdot \left(4{\cdot}6 \frac{V^2}{V_0^2} - 1\right).$$

The number becomes zero when $4{\cdot}6\,V^2 = V_0^2$. This merely expresses the condition that δ-rays of range ·2 mm. in hydrogen are the slowest that can be detected.

By taking the range of the α-particle to be proportional to the cube of its velocity, n can be expressed as a function of the range. The result is shown in fig. 1, where n is plotted against the equivalent range in air, for the last 7 cm. of range. According to our calculation, the number of δ-rays observed should increase slightly up to a point 2·46 cm. from the end of the track, thereafter falling off rapidly and becoming zero for a remaining range of 0·87 cm. This corresponds approximately to our experimental results. The initial increase in the number of δ-rays as the velocity of the α-particle decreases is so slight that a very large number of photographs would be necessary to establish it beyond doubt. The final decrease is, however, very striking, and is illustrated by comparison of figs. 1 to 6 (Pls. I. & II.) of tracks of α-particles of range in air between about 2 and 7·5 cm., and figs. 7 and 8, where the range is from zero to 1·3 cm. Fig. 7 shows a single δ-ray which is nearer the end of a track than any other so far obtained. If we suppose that the rare event of the closest possible encounter has occurred, we calculate from the range of the δ-ray that the velocity of the α-particle at this point is $1{\cdot}1 \times 10^9$ cm./sec.; calculated from the residual range, the velocity should be $\cdot 94 \times 10^9$ cm./sec.

The first casual inspection of the photographs led us to believe that the number of long δ-rays was disproportionately great. In examining the plates, however, there is a tendency to take those α-ray tracks which show long δ-rays as having been photographed under the best conditions, and to neglect others which, though equally sharp, show only short δ-rays. In so doing, no account is taken of the probability variation in the distribution of the long δ-rays. This is a very important factor, as is shown by figs. 5 and 6, where the α-ray tracks were taken under identical conditions. Fig. 5 shows a number of long δ-rays, while fig. 6 shows only short ones.

Fig. 1.



To investigate this point further, an analysis was made of the lengths of the trails of the δ-rays. Assuming as before that the range of a slow electron is proportional to the cube of its velocity, then on the simple collision theory the number of δ-rays of length greater than r, produced by an α-particle of given velocity, should be proportional to

$$\left(\frac{R}{r}\right)^{2/3} - 1,$$

where R is the length of the track resulting from a head-on collision.

The tracks in hydrogen were examined for a portion of the track from 1·84 to 3·06 cm. from the source, that is, for an average velocity of the α-particle of about 2×10^9 cm./sec. For hydrogen at N.T.P. the maximum range of the δ-ray

produced by such an α-particle is 2 mm. It was found that 157 δ-rays had ranges greater than ·62 mm., 51 had ranges greater than 1 mm., and 10 greater than 1·39 mm. These numbers are in the ratio

$$3{\cdot}1 : 1 : 0{\cdot}2,$$

while the theoretical ratio from the above expression should be

$$2{\cdot}1 : 1 : 0{\cdot}47.$$

In the case of helium the part of the track from 1·8 cm. to 8·0 cm. from the source was taken; 170 trails of δ-rays were found of length greater than ·47 mm., and of these 36 were longer than 1·03 mm. This gives a ratio of 4·7 to 1, while the theoretical ratio is 2·5 to 1.

The tracks in air and argon are not suitable for this analysis, owing to the short ranges of the δ-rays.

In both of the above cases it appears that the number of short δ-rays is relatively too great. The discrepancy is to be explained partly by the comparatively small number of δ-rays examined, and partly by the method of measurement. The lengths of the δ-rays were measured on the photographs, which are projections of a three-dimensional phenomenon. It is, of course, possible to reconstruct the track in three dimensions from the stereoscopic photographs, but this demands elaborate apparatus and would be a most arduous task. From the rough agreement with the simple theory which all our results show, it appeared to be unlikely that the results to be obtained in such a way would be a sufficient recompense for the labour involved. Moreover, for the sake of economy in photographic plates and in labour, the later photographs were not taken stereoscopically, but each half of the plate received a separate exposure.

It does not appear possible to apply an adequate correction for our method of measuring the lengths of the δ-rays, but it can be seen that such a correction would make our results more in accord with the theory.

It may be mentioned here that the results obtained by Bumstead in his electrical measurements of the δ-rays can be accounted for on the above theory of their origin. Bumstead measured the number of δ-rays of different energies emitted by a metal plate exposed to the δ-rays of polonium. As the metal plate was thick, the δ-rays observed were due to α-particles of different velocities. Taking an average velocity for the α-particle, it can be shown that the number n of

δ-rays of energy greater than T is given by

$$n = \frac{a}{\mathrm{T}} - b,$$

where a and b are constants. This relation expresses Bumstead's results rather better than the empirical formula he proposed, and the ratio a/b of the constants, deduced from his experiments, agrees approximately with the value calculated from the theory.

The next point we have to consider is the direction of emission of the δ-particles. C. T. R. Wilson came to the conclusion that in air the δ-rays had, on the average, no component of velocity in the line of motion of the α-particle. The present experiments have confirmed this for δ-rays in air and argon. In hydrogen and helium, however, the δ-rays undoubtedly have a velocity component in the direction of motion of the α-particle, in particular those δ-rays of long range. This is well illustrated by fig. 1 of Pl. I.

This difference in the apparent direction of emission is due to the fact that the scattering of the δ-rays is greater in heavy gases than in light. The scattering, even in hydrogen at low pressure, is too great to permit of any detailed correlation of the lengths of the δ-rays with their direction of emission. There is little advantage to be gained by reducing the initial pressure of hydrogen in the expansion chamber below about 12 cm., owing to the great stopping-power of the water-vapour which must of necessity be present. In the case of hydrogen at N.T.P. it can be shown that the most probable number of deflexions through an angle greater than 45° in the first 0·2 mm. of a 2-mm. δ-ray is 0·7, and in the first 0·3 mm. of a 0·6-mm. δ-ray it is 5·4. Thus the longer tracks should, as has been found, have a forward direction. In air, however, since the range of a δ-ray of given velocity is only 1/5 of the range in hydrogen, and the number of scattering electrons and the charge on the atomic nucleus are each some seven times as great, the chances of deflexion through a large angle are so greatly increased that the δ-rays will emerge from the α-track at random.

Some photographs of tracks in hydrogen were taken with a magnetic field of about 400 Gauss acting at right angles to the track, and along the axis of the expansion chamber. This field was obtained by passing a current of about 20 amperes through a coil resting on the top of the expansion chamber. The idea was to test whether any

appreciable number of δ-rays was emitted in the direction of motion of the α-particle. The presence of such rays would not be detected in our previous experiments. The magnetic field, however, was sufficient to bend them out of the path of the α-ray and so make them visible. No change in the number of δ-rays was noticed, indicating that even in hydrogen the scattering is sufficiently great to bring the fast δ-rays out of the α-particle track. Fig. 4 shows an α-ray track taken under these conditions. The curvature of the two long δ-ray trails is plainly seen.

One further point may be mentioned. If an electron is ejected from the K level of an atom traversed by the α-particle, we should expect the corresponding X-radiation to be emitted when the atom returns to its normal state. This X-radiation will be absorbed in the gas in the neighbourhood and give rise to a β-ray of very short range, corresponding to the energy of the K level. Wilson has already pointed out that such β-rays can be observed very close to the early portion of an α-ray track. In air their range is so short that only a minute globular speck is visible. In argon, however, the trail of such a β-ray should be about ·3 mm. in length, for the energy of the K level is about 3000 volts. On the other hand, this event will occur very seldom, for almost a head-on collision of the α-particle is required to remove an electron from the K level of argon. We have in a few instances succeeded in observing a β-ray trail of this length in the neighbourhood of an α-ray track in argon.

Summary.

The tracks of α-particles in four gases—viz. hydrogen, helium, air, and argon—have been obtained in a Wilson expansion chamber, and the production of δ-rays along them has been studied.

As far as our observations go, the results are in accord with the view that the δ-ray arises from the collision of the α-particle with an electron in the atoms through which it passes. We assume that, for the distances involved in these collisions, the α-particle and the electron behave as point-charges, and that the law of force between them is that of the inverse square.

Photographs are reproduced to illustrate the various points discussed in the paper.

II. *Models of Electron Structure, Quantum Action, and the Gravitational Field.* *By* W. M. Thornton, *O.B.E., D.Sc., D.Eng., Professor of Electrical Engineering in Armstrong College, Newcastle-upon-Tyne* *.

1. *Introduction.*

THE following notes were given to students of electrical engineering to suggest, by the aid of models, a picture of an electric structure of matter. They make no pretence to be more than a rough mechanical scheme based on the assumption of a vortex filament æther of which each element has torsional elasticity. The existence of such a filament implies a basic twist, in this case probably dynamic. The suggestion now made is that electrons and protons are produced by applying to it left- or right-handed twists, the effect of which is in the one case to unwind the original torsion, in the other to increase it and form a densely-packed thread. In the process, loops are formed which are either electrons or protons. Once formed in a medium with the properties of a fluid, they persist. Whittaker remarks that, of all the theories of the æther, the vortex filament or sponge has the greatest interest.

An indiarubber cord has torsional rigidity but no intrinsic twist, so that right- and left-handed loops are, with it, of the same size. The models can be made from closely-wound spirals of wire ; but though there is then a clear difference in the size of right- and left-hand loops, it is not possible to approach that which exists between protons and electrons.

The notes were given at different times, and a certain repetition of statement could not be avoided.

2. *Protons and Electrons.*

The form of the electric bond between nucleus and electron of the hydrogen atom is not yet known ; but it is possible to construct a model of it from the evidence of the behaviour of electric charge in motion, and through it possibly to explain quantum action. Any mechanical scheme can be made to work if the appropriate forces are assumed. In the present attempt there is only one essential, the existence of a vortex filament æther, which can be twisted or untwisted to form protons or electrons and which carries gravitational forces. The magnetic field around a moving charge is such that when the charge is positive the flux is right-handed, when

* Communicated by the Author.

negative left-handed. This is one of the key phenomena of nature, and suggests in the strongest way that the positive unit has the physical characteristics of a right-handed screw (such as a propeller), a negative charge of one left-handed. The simplest representation of such a screw is a half-turn

Fig. 1.

PROTON

element (fig. 1), which may be regarded as formed on a line or tube of force. Such an element moving loop first in the direction of the arrow, like a ship's log in a material medium, would by its reaction turn right-handedly or set up a right-

Fig. 2.

ELECTRON

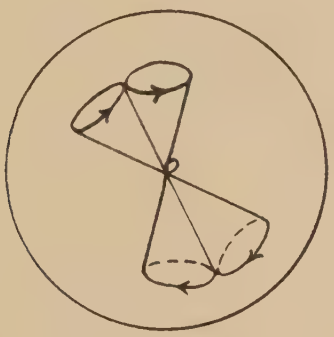
handed strain in the towing-rope, and a left-handed element (fig. 2) would turn in the reverse direction, the twist being in

each case proportional to the velocity of motion, in this way imitating the direction and magnitude of the magnetic fields around moving charges. The phenomena of steady current flow do not require anything more complex than these models, but in order that they should exist permanently as structural parts of matter and differ in size, the tubes of which they are composed must have intrinsic twist. Any such cord held at one end and turned right-handed at the other will form fig. 1, left-handed, fig. 2.

The field of force known to diverge uniformly from a point-charge can be imagined to spread from a kink of this kind by uniform enlargement of a tube of force in proportion to the radius.

To visualize a three-dimensional static twist, take a spherical ball and twist a conical element of the surface to the centre around a diameter to the opposite face until a kink forms at the centre (fig. 3). The charge would then be

Fig. 3.



an assembly of these loops, and the elements, if put together under torsion and set free, would lock into a permanent state of twist. A spherical distribution of stress from a vortex filament loop as a unit of charge seems to require that each filament should be subdivided into many elemental threads, each enlarging its section from the centre. There may truly be a finite number of tubes of force from every unit of charge. Not more than six would be stable if arranged symmetrically around the centre of a filament. In the vicinity of the centre the inverse square law could not hold.

It is a necessity of electrostatic theory that at a distance from the charge such that the inverse square law holds the field must have everywhere the same magnitude and sign.

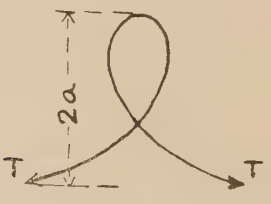
That is, every element of surface on a sphere with a positive charge at the centre has a right-hand twist of the same intensity. The only way of making a vortex filament do this is by giving it the half-turn of figs. 1 and 2. Such a configuration would obey, at some distance from the centre, all the laws of electrostatics.

3. *The Shape of Electrons and Protons.*

An elastic wire bent into any of the forms of the elastica curve can be rotated freely about its own axis without change of shape of the curve. Kirchhoff showed that the static elastic problem is analogous to motion about the centre line of the wire, the moment of momentum then corresponding to the couple about the axis in the static case. The vortex filament electron is stable provided that the twist is maintained. There is also in the fluid vortex case an effect which makes for stability of form that does not exist in the kinetics of solids.

When two vortex filaments cross at right angles, the fluid rotating around one axis can at the point of crossing be caught by the other vortex, and form a complete path about both, acting as an elastic band holding the branches together. It is conceivable that the permanence of an electron or proton loop may depend upon this.

Fig. 4.



The form of the loop (fig. 4) is similar to that of the simple elastica (fig. 6, p. 148, vol. i. pt. ii., Thomson and Tait, Nat. Phil.). From the equations given there the maximum ordinate of the loop is $2a$, where $a = \left(\frac{EI}{T}\right)^{1/2}$, E being the elastic coefficient of bending, I the geometrical moment of inertia of the section of the filament, and T the tension in it. If, as is suggested in § 19, the filament is a spiral vortex, the tension is the rate of change of momentum along the axis.

4. *Why Opposite Charges attract.*

The space around a positive charge is, in the model, considered to be in a state of right-handed twist (fig. 1). A free positive charge entering this space could not link up—the circulations are in opposite directions and could not coalesce; but such charges, if formed on the same filament or held in position by the presence of negative charges, might conceivably remain connected in equilibrium.

If one of two opposite charges is attached to a surface, it has an external field in which the other tries to turn. When a charge turns, it advances from pole to pole like a nut along a screw, away from a similar charge towards an opposite charge, setting up as it goes in the surrounding medium an induced magnetic field proportional to the velocity of motion. The model of fig. 1 would be driven loop first in such a field in one direction, that in fig. 2 loop first in the reverse direction.

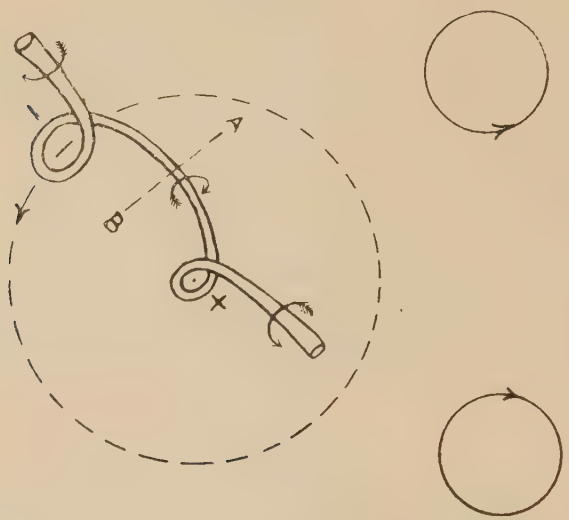
Another way of viewing this is to imagine a thin membrane (AB, fig. 5) dividing a fluid into two parts in each of which there is a vortex terminating on the membrane in a vortex sheet. If the circulation is in the same direction in the two parts and in line, withdrawing the membrane will unite the vortices, loops on which will then be attracted. If the circulation is opposite in the two parts, they will move away from one another sideways.

5. *Linkage in a Hydrogen Atom.*

Right- and left-handed elements can be joined by a tube of force becoming common to both. A well-known illustration of electrostatic stress is a state of twist of tubes of force between oppositely-charged surfaces. Fig. 5 shows right- and left-hand kinks on a thread representing the attachment of positive and negative charges, which will not together be a permanent force unless either one is held in position as in a massive atom by the presence at the nucleus of other tubes of force which form the complete spherical field, or by motion in space. The revolution of a negative electron loop first about a proton as nucleus causes the loop to twist left-handed and so prevent the filament joining the charges from folding back. Unless the circulation at the crossing-point is sufficient, it would be necessary for the stability of a free atom made on such an elastic system that the negative charges should be in motion around the positive. The Rutherford-Bohr type of atom is then necessary for the stability of matter.

The nuclei of atoms are known to be extremely small and difficult to move ; electrons are light and mobile. The model illustrates these properties, for if any cord or spiral of wire having a right-hand pitch is turned right-handed, the lood formed is small and tightly held ; turned in the reverse direction, it is large and open. The difference in size and behaviour of the two fundamental electric charges implies that the æther has an intrinsic twist such that an added right-handed torsion causes condensation, left-handed, expansion.

Fig. 5.



In the above model the positive kink has a free end, so that a hydrogen atom can hold or capture another free electron as required on Bohr's theory for the continuous spectrum of hydrogen. The section of the filament is probably not constant, but enlarges at the centre in the manner of the lines of flow between a source and sink.

6. *Absence of Magnetic Field of Single Orbit.*

Tubes of force, whatever their ultimate nature, cannot be bent without reaction. It follows that in fig. 5 the positive and negative charges cannot approach indefinitely, and the inverse square law which holds when the charges are so far apart that the tubes joining them are nearly straight, fails and becomes one of repulsion, according to a higher power than the second when they are close together. The inverse

square law is known to hold within the atom, but not near the nucleus.

When an electron revolves around a proton to form an atom of hydrogen, it also follows from the figures that the loops must lie in the plane of rotation. On the preceding view the revolving electron loop in a hydrogen atom tries to rotate, but is prevented from doing so more than a very small amount by the stiffness of the tube of force joining it to the nucleus. There is therefore *no magnetic field* and no continuous absorption of energy produced by such a motion, for the usual rotational strain around a negative moving charge cannot be established. The Rutherford-Bohr hydrogen atom in spite of its orbital motion is non-magnetic.

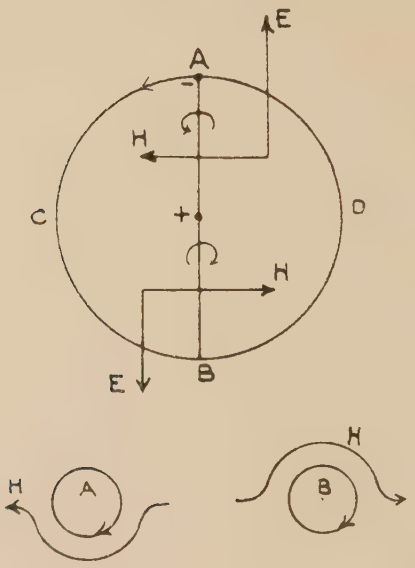
7. *Reaction of Radiation on Atomic Field.*

The electric field of radiation in free space is in the wave front, and the magnetic field at right angles to the electric. When the energy of such radiation is absorbed by an atom of the kind considered there are certain restrictions to change of motion of the electron. For stability of the orbit radial harmonic oscillations cannot occur, and those that under certain circumstances can occur perpendicular to the plane of the orbit have small energy and are not such that they could increase the diameter.

Absorption of energy occurs when the frequency of the incident radiation is that of rotation of the electron, or is related to it by the laws which govern the frequency of spectra; but since it is impossible to work up a radial oscillation even with synchronism, it would be necessary to give the energy quantum in one revolution or not at all. (It is, indeed, simpler to regard the relation $W = h\nu$ as written $\frac{W}{\nu} = h$; that is, the energy which can be absorbed or radiated during one complete rotation is the same at all frequencies.) Either the absorption must take place in one period, or there must be some mechanism by which the action may be worked up without the radius slowly changing. The former alternative would seem to be ruled out, for even with the most intense natural fields of the order of 10 volts a centimetre, an electron could not acquire a quantum of energy in one revolution by the electric forces acting upon it in the wave front. In the model an electric field normal to the plane of the orbit does not influence the motion even if the periods coincide. When it is in the same plane there is no effect until the incident radiation synchronizes with

the revolution of the electron about the nucleus. There is then a series of unidirectional tangential forces repeated each half revolution—a rectified sine wave ; but according to quantum action, there is no acceleration of the electron. When the orbit is in the wave front of the incident radiation, the magnetic component is at one position along a radius, after a quarter revolution across it. If the radial bond to the nucleus is a magnetic vortex filament, the influence of a stream past it is to exert a rotational drag upon it, since there is no slip, retarding the spin if below a certain speed,

Fig. 6.



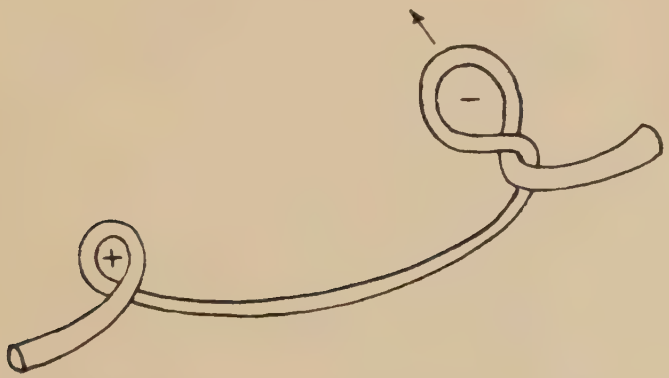
accelerating it if greater. When the radiation reaches a certain frequency, the radial bond begins to be wound up by a kind of ratchet movement—that is, its twist is increased—until it reaches a critical value, at which a change of position occurs according to quantum laws. The Poynting flux of energy is converted from the linear stream of the advancing radiation into the increased spin of the filament ; but it cannot enter the filament in this way unless the electric component of the field is in the plane of the orbit. Energy is absorbed in a series of unidirectional pulses each lasting half a period. Fig. 6 illustrates this. At C and D there is no action if the radiation is polarized as

shown at E. The application of a magnetic field cannot have permanent effect on such an atomic structure unless it lasts only for a half period of rotation of an electron about the nucleus, an inconceivably small interval of time which cannot be realized experimentally.

8. *Mechanism of Quantum Action.*

In the previous section it is shown that the electron of a hydrogen atom is, in effect, *wound up* by synchronous radiation, in the sense that the twist of its bond to the nucleus is intensified. Fig. 5 now provides a clue to the quantum action in the connexion between radiation and matter, for if the twist on such a cord is increased to a certain critical amount, the negative loop makes suddenly a complete turn, taking the position of fig. 7. The increased energy of twist

Fig. 7.



causes a sudden change of position, and the radius is held constant until such a change takes place. When the incident radiation ceases, the kink returns to the normal position, so that the persistence of incident radiation is necessary for continued activation.

It is readily found by trial that such a double twist straightens the bond, so that at the moment it occurs the orbit enlarges, though under the limitations of a model not to anything like the four times greater radius required by Bohr's quantum theory. What the initial curvature of such a bond is likely to be and how far it is extensible under a straightening force is conjecture, and the kink can conceivably move along the tube, but the type of movement is that looked for.

The model explains why the incident radiation may be exceedingly weak and yet absorption take place in quanta as in the photoelectric effect; why the effect is dependent upon frequency; and why the radiation from an atom must always occur in quanta as the twist relaxes a revolution at a time, for radiation can only occur in quanta if *the negative kink is compelled to lie always in the same relation to the plane of motion.* There is no question of dissipation of energy by friction, and the configuration is such that the electromagnetic resistance to motion is a minimum. This is when there is no circulation through the loop of the kink. The latter places itself with its plane in that of the motion, and in this position there is no resistance. According to the model, the electromagnetic radiation arising from a sudden decrease of radius is set up by the corresponding relaxation of the filament connecting proton and electron. The change of the electrostatic energy of the two charges is transmitted into space by the equal magnetic impulse in the circulation of the filament joining them. This magnetic movement is at right angles to the electric field between the charges, and therefore in the right position to start a wave motion of regular type.

The photoelectric emission of electrons from metals in quanta relations is a trigger effect. The outer electrons of atoms in metals are very closely packed, and in a state of mutual repulsion such that the stability of some of them is easily disturbed. Anything that does this may result in electrons being set free, and this is continually happening. The magnetic field of radiation, or that of an electron passing close to or through an atom, resembles in its effect on the filaments between protons and electrons a hand swept over the strings of a harp, throwing them into lateral vibration and possibly snapping one, the released energy of which is much greater than that required to break it. A broken string is analogous to the release of an electron with the collapse of the bond to the nucleus. The energy of the released electron comes from the atomic structure, not so much from the incident radiation.

9. *Vibrations with Zero Energy.*

In the development of the Planck's radiation formula it is considered that of M vibrations, N have zero energy.

The fraction $\frac{M-N}{N}$ is that proportion of the whole

number which have any energy; and this is proved to be $\epsilon^{-e/RT}$, where e is a quantum, R and T the gas constant and temperature.

From this it follows that "in a red-hot mass of iron less than 1 per cent. of the red vibrations have any energy; the remaining 99 per cent. are perfectly dead" *.

Of all the statements in the quantum theory this is perhaps the most difficult to reconcile with the old view. Interpreted by the model, it means not that the vibrations are dead, but that it takes 99 vibrations to get one quantum of energy absorbed. It takes so many revolutions or alternations of the field of radiation to wind the electron loop up to the point where it turns over suddenly once to form fig. 7. There are 99 vibrations in which there is no evidence of absorption or radiation of energy.

10. *Mass of Protons and Electrons.*

On the vortex sponge theory, or any theory in which an æther at rest is postulated of which protons and electrons are individual parts, matter is in continuous flux. No proton or electron in motion is ever composed of the same æther for more than an inconceivably small portion of time. If the laws of vortices hold for the æther filaments considered, a region of small tightly-bound loops has higher angular velocity and greater resistance to motion than one in which the section is greater or the loop with less curvature—that is, its inertia is greater. A large open loop moves easily by comparison. The difference in mass and dimensions of the two charges is so great that the apparent elastic constants of the filaments must differ greatly in degree from those of ordinary matter. If they could be determined from the properties of atoms on this or any model, they might give a clue to the value of the absolute dielectric constant of free space.

The suggestion that a quantum consists of energy stored by a second further twist of a filament as in fig. 7 has, in consequence of the above, the effect that the added twist increases the apparent mass of an electron or gives it to some extent the character of a positive charge; and this may account in part for the departure of atomic weights from integers. If this were so, it would account for the weakening of the bond to the nucleus and the enlargement of the orbit according to a square law. Presumably a point would be

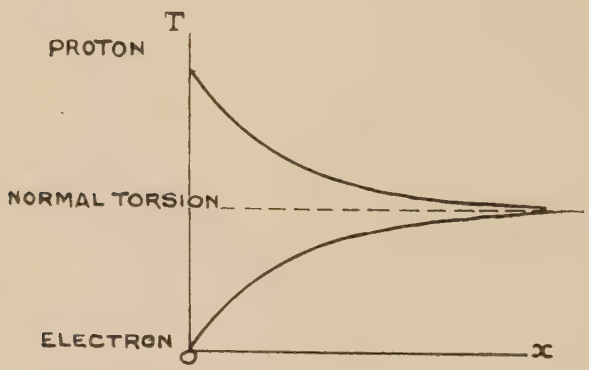
* Jeans, 'Report on Radiation,' p. 31.

reached where the attraction to the nucleus would be unable to hold the electron so that there would be a limit to the size of the hydrogen atom. Intense radiation would seem to be the only controllable means of splitting a hydrogen atom.

11. *Mass of Protons and Electrons* (continued).

The view advanced in the previous sections is that the fundamental charges differ in the first place in the direction of a twist superposed upon a normal torsion of an æther filament, that of the proton being the greater, that of the electron less. This twist in a single thread must be regarded as greatest at the centre, as in a waterspout or vortex, or at the surface of a hollow vortex. Assuming the intrinsic torsion to be T_0, and the maxima of the added or subtracted twists to be the same, as they must be if connected by a

Fig. 8.



common tube, and equal to T_1, the twist at any distance x from the axis of the filament, assumed straight, is $T_0 - T_1\epsilon^{-\alpha x}$ in the case of the negative or less dense charge, $T_0 + T_1 e^{-\beta x}$ for the dense proton filament (fig. 8).

Near the axis the ratio of these is $\dfrac{T_0 - T_1}{T_0 + T_1}$.

This, other than direction of twist, is the essential difference between them.

If, then, we may assume that this is the cause of difference of mass and that the ratios of their masses are the same as of their concentration or vorticity,

$$\frac{T_0 + T_1}{T_0 - T_1} = 1845, \quad \text{or} \quad T_1 = \frac{1844}{1846} \cdot T_0.$$

The meaning of this near approach to unity is that the left-handed twist, to which the structure of the electron is supposed to be due, almost negatives the normal twist T_0 so that the æther in the electron is held in very light torsion. An electron has more form than substance. The same twist that causes so light and mobile a structure makes, on this assumption when reversed, one 1845 times as massive. Since T_1 is nearly equal to T_0, the torsion of the proton is *double* that of the normal filament. On the analogy of ordinary matter the elastic coefficient of the æther is such that doubling the twist of an element of it has the same effect as doubling its density. An electron is a region of lowered density, a hollow or nearly unstrained thread approaching Kelvin's hollow spiral vortex filament.

The exponential terms are introduced, for at great distances the added spin vanishes, leaving only the normal torsion T_0 in free æther filaments.

12. *Why Electrons are freer than Protons.*

On the vortex filament theory, the more intense the circulation the greater the "suction"—that is, the field in the immediate neighbourhood of a positive charge is more intense, because of its smaller size, than that around a negative charge. In all cases beyond that of the hydrogen atom where the bond is the simplest conceivable, the presence of the diffused field from other outer electrons attached to the nucleus makes it easier for an electron to escape; and in metals one must regard the forces of repulsion from these electrons as so high that they escape and interchange with ease.

13. *Cohesion and Gravitation.*

Since all matter is now found to be electrical, cohesion and gravitation must be capable of interpretation by models of this kind. On the assumption that the bond from nucleus to electron does not utilize all the tubes of force from each, or that, as in fig. 5, there is a free end to the proton, the field from one atom to another which causes cohesion is merely the drawing together of molecules so that the vortex filaments of their atoms become common to both; and since there is no restriction to the number which can be attached in line, we may regard the matter of the earth as a succession of molecules or of atomic nuclei threaded on common filaments reaching to the centre, each nucleus contributing to the inertia of the whole, and each filament being capable of sustaining the load or tension of all its atoms.

In order that gravitation should be explained in this way, the filaments must be considered to be capable of infinite extension, not like an elastic cord, but in the same way as a bullet passing through the air causes a spin of the latter around it so we may regard the movement of a planet from a sun as setting up as it goes to its orbit a state of an enormous number of persistent twists which in this case cannot relax except by the return of the satellite. Thus space near the sun is not undisturbed æther, but a mass of threads permanently twisted by reason of the gravitational field of each planet. Such a state of the medium, though not actually constituting matter, is an extension of it, and might affect the passage of light at grazing incidence through it.

Gravitational tubes of force need not end on solid matter ; they can terminate by dilution in the vortex filaments of free space. An isolated body from interstellar space could then carry with it its own gravitational field and be affected by another body which it may pass. The essential torsions in the æther around such a free body are a consequence of the original cataclysmic twist to which in § 18 the origin of the body is attributed.

The vortex filaments of which the kinks of figs. 1 and 2 are part are the means by which gravitation is transmitted. Electricity is, in fact, a singular form of gravitational space ; only in interstellar space is the æther an unstrained vortex sponge, and even there it is not at rest, for radiation is continually passing and each thread is in continual spin about its axis.

14. *Chemical Combination and Gravitational Force.*

Most of the chemical and physical properties of an atom depend upon the outer electrons, but gravitation, depending only on mass, upon the protons. In the model of fig. 5 there are free ends to the electron and proton loops. The former is the chemical bond, the latter the gravitational. Gravitational forces are transmitted through matter by links in a chain. A gravitational field at the surface of a body is attached to the free end of protons which are linked to their electrons. These in turn are attached to other atoms by the chemical bond—that is, by interlinking of orbits or by an electron becoming attached to two nuclei. Fig. 9 illustrates how such forces may be transmitted through matter.

The bonds of chemical combination are part of the means by which gravitational force is transmitted in solids ; another part is cohesion. In the organic world cohesion is largely the interlocking of cells, in the inorganic world of crystals. Liquids and gases experience gravitational forces by the free ends of their proton loops engaging with, breaking away from, and re-engaging gravitational tubes of the body to which they are attached in space.

15. *Existence of Electrons in the Nucleus.*

There is no experimental evidence of the existence of free units of positive charge except in the rare and transient case of atoms expelled from a radioactive body, and even then there may be electrons in the nucleus. This implies that they have so great a structural affinity for electrons that they always have one at least attached to them ; and since free electrons exist, it seems improbable that positive units at rest ever can be free —they are all absorbed in the structure of matter. But it is possible from the model for an electron to be linked to two protons (fig. 9) and in this way be held in

Fig. 9.

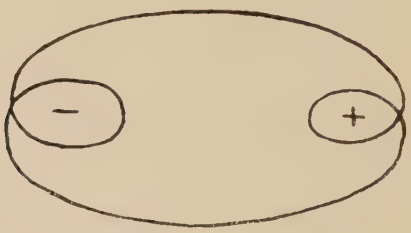
the nucleus, though under such intense force, due to the high curvature of the "elastica" bond, that when they are expelled by the shock of high velocity bombardment or in radioactivity they emerge with great speed. It is conceivable that a simple atom may be formed, like a benzene molecule, of a chain of these charges forming a closed ring. Such a nucleus would be very inert, since it has few, if any, divergent lines or tubes of force.

Although positive or negative charges, if free, repel those of the same sign, yet one can conceive a series of them formed on the same filament in the same way that such a series of loops can be formed on an elastic cord, all of the same right- or left-handed twist. In this way an extremely dense body might be formed with few or no electrons.

16. *A Model of the Helium Atom.*

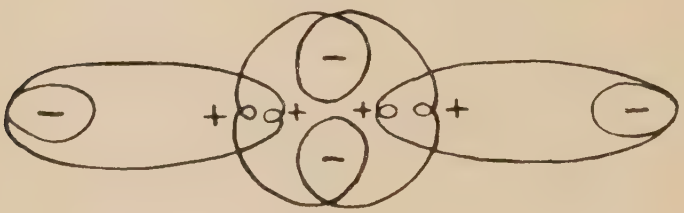
A helium atom differs greatly in physical and chemical properties from hydrogen. If a hydrogen atom formed a closed loop (fig. 10) it would have little or no chemical

Fig. 10.



affinity as measured by the existence of free active ends to its filaments. For this reason the structure of fig. 5 is preferable. But a helium atom is so entirely inert that a model with linked closed loops is suggested (fig. 11).

Fig. 11.



Here the positive charges in the nucleus are drawn together by the centrifugal pull of the outer electrons, but are held apart by their own repulsions forming a stable system; and since there are also two negative electrons in the complete four-proton nucleus, the atom would be composed of two large loops with their positive charges inside and two hydrogen atoms in series forming the smaller inner loop. The radius of a helium nucleus is, in fact, equal to the diameter of a negative electron as the model suggests.

The outer electrons can be lost without the disintegration of the nucleus, for the two inner protons move nearer to the centre when they go. The atom in this state may have intense chemical activity since it has unsaturated bonds. Could, for example, molecules of helium chloride ever be formed by exposing chlorine to radioactive action?

The two-group spectrum of helium has been traced to the

two outer electrons moving in orbits slightly inclined to one another. The model of fig. 11 would give such a spectrum, for loops so linked cannot lie in the same plane everywhere, though the outer loops might nearly do so.

17. *Radioactivity and the Helium Atom.*

The projection of a helium atom from the nucleus of a radioactive body implies the existence of forces in it resembling those of static or dynamic deformation suddenly released. Atoms of the hydrogen type can pack into a symmetrical system easier than the suggested helium atom with interlinked loops. It is conceivable also that in the packing of a dense atom like radium the helium links may be displaced so that the outer electrons are not exactly opposite. There is then a resultant force away from the centre. A complex nucleus of such units resembles those puzzles composed of loose metal parts which in one slightly strained position can be separated.

A further possibility is that the helium atom is normally incomplete—that is, with some of its loops open and attached to other charges in the nucleus. At some stage of the slow rearrangement of charge that undoubtedly occurs these ends break from their hold and close. At this moment the helium atom becomes a foreign body having no part in the structure, and is expelled by the closing up of the bonds around it in their effort for symmetrical spacing.

18. *Mode of Generation of Electric Charges.*

If an element of volume of a vortex filament æther is thrown into intense rotation *as a whole*, the circulation of some filaments will be increased, of others diminished. At a critical value of this added twist, loops are formed in the manner of § 1, lock into shape, and the two kinds of electricity appear, combining immediately to form matter. Immense spiral turbulence or the electric and magnetic fields of radiation of great intensity are possible sources of the generation of matter as known to us. A new world may leap into being by an intense swirl in the æther causing its filaments to precipitate out as electricity and matter to form a new spiral nebula or star. It is a consequence of such an action that equal numbers of protons and electrons should be produced; but it is possible that before such newly-formed units could combine, the electrons might be swept away by the terrific motion. In such a case a body of immense density would be formed; and since there would

be no electrons to vibrate and radiate, the star or nebula would be dark. It would be stable, for it is formed *in situ* and not assembled. Once formed, the protons are inextricably tangled and could not well escape ; but if they should, the star would explode with great disturbance of the æther and liberation of energy as light and heat to form a "nova."

19. *Faraday's Law of Electromagnetic Induction.*

The hydrogen atom is the unit of matter—a proton and electron connected by a common bond. Such a unit moved across a steady magnetic field is polarized in the sense that there is a radial electric field ; but there is no corresponding movement of the charges except under quantum conditions. The influence of the induced electric field can be illustrated by its action in fig. 5. The internal field is there shown as the twist of the common tube of force. An induced field either increases or decreases this twist, and should therefore have a rotational component (Heaviside's G in curl E $= 4\pi G$). According to this the intrinsic twist of æther filaments is identified as a magnetic circulation probably very slow, as shown by Lodge, and an electric charge is merely a kink in a magnetic vortex filament. But in order that there should be a true magnetic circulation, there must be a displacement equivalent to a current along the axis of the filaments. If the motion of a filament were spiral this would be satisfied ; an axial component of motion combined with a circulation around it. Faraday's Law of Electromagnetic Induction reduces in the model to the statement that when an element of space and a magnetic field are in relative motion, the vortex filaments experience a superimposed twist, screwing, if matter is present, the protons to one side, the electrons to the other.

20. *A possible Magneton or Unit of Magnetism.*

The electric current along the axis of a vortex in the electromagnetic analogue of the liquid case is the same in both electron and proton, since these can be linked by a common tube. This current in passing around a loop has a definite field linked with it. Is such a unit of magnetism the suggested magneton? The fields of such loops are part of the flux around a magnetic vortex filament, and are extremely small and local. A single hydrogen atom might have a stray field from the proton loop to the electron, but most of the flux would be close to the loops. The sign of the flux through the proton loop is the same as that which would be caused by the spin of the electron about its line of motion if

it could occur. The sign of the electron loop flux is opposite to that of the proton, so that, except for any stray field connecting the two, the atom would be non-magnetic.

For a substance to be magnetic there would have to be the same orientation of a large proportion of densely-packed protons, and from the small range of magnetic materials it is probable that such orientation is only possible in a few cases. From fig. 3 it will be seen that, according to the model, a magnetic field should have the effect of rotating a free charge in a plane at right angles to the field. On ordinary matter containing equal numbers of electrons and protons a magnetic field has no resultant effect.

21. *Diameters of Vortex Filaments.*

An estimate of the order of the diameter of an æther filament may be made from the dimensions of electrons on the assumption that they are loops of the kinds considered. The constant a in fig. 4 is $\left(\frac{EI}{T}\right)^{1/2}$. For a solid round wire $I=\pi r^4/2$, and for a vortex filament is of the same order. Analogy with a hollow vortex is more difficult. The radius r of the filament has two limiting sizes—that of the electron larger, of the proton smaller, than the normal filament of free æther. These are determined by the size of the loop, the overall dimensions of which are $2a$. By comparison with loops on wire spirals the diameter of the filament cannot well be greater than $0{\cdot}5a$, and a radius of $0{\cdot}25a$ can be taken as a first estimate.

The size of the helium nucleus is about $4 \cdot 10^{-13}$ cm., and in this there are two electrons. Unless the size of an electron varies with the intensity of the forces acting on it, its diameter there is of the order $2 \cdot 10^{-13}$ cm. Taking this as $2a$, the larger possible radius of a filament is not greater than $2{\cdot}5 \cdot 10^{-14}$ cm. There are in the helium nucleus four protons. If these are grouped as in fig. 11 their maximum diameter is 10^{-13}, but they are probably much less.

Taking, in fault of a better supposition, the mass of a charge to be inversely proportional to its volume, the ratio of the mass of a proton to that of an electron is $(I_e/I_p)^{3/2}$ and $r_e/r_p = 1845^{1/6} = 3{\cdot}5$.

According to this the effective radius of the filament of a proton is $1/3{\cdot}5$ that of an electron, or at most $0{\cdot}7 \cdot 10^{-14}$ cm., the elastic constant and tension being the same.

The radius of a filament of free æther is between these. If the absolute density of æther is the mean of that of electrons and protons, the diameter of its filaments is on the above argument about $2 \cdot 10^{-14}$ cm.

III. *A Method for Determination of the Adsorption of Ions on Colloidal Particles by means of Donnan's Membrane Equilibrium Theory.* *By* HERMAN RINDE *.

DONNAN'S Membrane Equilibrium Theory can be stated as follows: If there are on one side of a semipermeable membrane (inside the membrane) non-dialysable ions, this will lead to an unequal distribution of a dialysable electrolyte on both sides of the membrane, so that at equilibrium the activity of the electrolyte inside the membrane is equal to the activity of the electrolyte on the other side of the membrane (outside the membrane). If there is only one dialysable electrolyte with two monovalent ions, the activity is equal to the product of the activities of both ions. If a_{1+} a_{2+} are the activities of the cations inside and outside the membrane, and a_{1-} and a_{2-} the activities of the anions, we have

$$a_{1+}\,a_{1-} = a_{2+}\,a_{2-} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let y be the concentration, f_y the activity coefficient for the cations inside the membrane, w and f_w the same expressions for the anions, and let z denote the concentration of the nondialysable ions. Then

$$a_{1+} = f_y\,y \;; \quad a_{1-} = f_w\,w. \quad . \quad . \quad . \quad . \quad (2)$$

As the liquid inside the membrane must be electrically neutral, we obtain, if the nondialysable ions are assumed to be anions,

$$y = z + w. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus

$$z = \frac{a_{1+}}{f_y} - \frac{a_{1-}}{f_w} \quad . \quad . \quad . \quad , \quad . \quad . \quad . \quad (4)$$

Substituting from formula (1)

$$z = \frac{a_{1+}}{f_y} - \frac{a_{2+}\,a_{2-}}{f_w\,a_{1+}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The activity of the different ions is not exactly known †, but for hydrochloric acid it is probable that the difference in the activity coefficients between the hydrogen and the chlorine ions is not large. It may therefore be permissible to calculate with the same activity coefficient for both these ions. Further, if the concentration of the nondialysable ions is

* Communicated by Prof. F. G. Donnan, F.R.S.

† Lewis and Randall, 'Thermodynamics,' p. 379.

low, the activity coefficients f_y and f_w can be replaced by a mean value f, which is equal to the activity coefficient of HCl outside the membrane. As it is supposed that there is no other electrolyte than HCl outside the membrane, we can write

$$a_{2+} = a_{2-} = a_2,$$

and if a_1 is written instead of a_{1+}, formula (5) can be simplified to :

$$z = \frac{a_2}{f}\left(\frac{a_1}{a_2} - \frac{a_2}{a_1}\right). \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If the nondialysable ions are cations, this formula becomes

$$z = \frac{a_2}{f}\left(\frac{a_2}{a_1} - \frac{a_1}{a_2}\right). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It is therefore possible to calculate the concentration of the nondialysable ions from the activity coefficient for HCl and the experimental determinations of the hydrogen ion activity inside and outside the membrane. In this research I have used the values of the activity coefficient from Lewis and Randall ('Thermodynamics,' p. 336), and from a curve with f as ordinate and ionic activity as abscissa, values of f, corresponding to the hydrogen ion activity a_2, can be obtained. The values of f and a used are reprinted in Table I.

Table I.

a.	f.	a.	f.
0·0005	0·99	0·043	0·86
0·001	0·98	0·081	0·81
0·002	0·97	0·157	0·78
0·005	0·95	0·230	0·77
0·009	0·92	0·305	0·76
0·018	0·89	0·381	0·76

This Membrane Equilibrium Theory has been experimentally tested by Donnan and his collaborators, J. Loeb, Procter and Wilson, and many others *. In all these researches

* For a complete bibliography on the subject see W. E. Garner, "Membrane Equilibria," Fourth Report on Colloid Chemistry, p. 121 : London, 1922 ; F. G. Donnan, "The Theory of Membrane Equilibria," Chemical Reviews, vol. i. No. 1, p. 73 (1924).

it is considered that an ion is nondialysable only when its own dimensions are so large that it cannot pass through the pores of a semipermeable membrane. One can, however, imagine that a dialysable ion, through adsorption to a nondialysable colloidal particle, becomes nondialysable. z, in the preceding formulæ, signifies then the concentration of adsorbed ions. As is known, the colloidal particles of a great many colloids are electrically charged, and it is supposed that this charge and the stability of the colloid are due to the adsorption of ions.

Donnan has shown that there must exist across the membrane a potential difference (the membrane potential), and that the value of this is

$$E_m = \frac{RT}{F} \log \frac{a_1}{a_2}.$$

Formula (7) can therefore be transformed to

$$z = \frac{a_2}{f}\left(e^{\frac{E_m F}{RT}} - e^{-\frac{E_m F}{RT}}\right). \quad . \quad . \quad . \quad . \quad (8)$$

Thus, from the membrane potential and the concentrations of the ions outside the membrane, it is possible to calculate the quantity of adsorbed ions.

The osmotic pressure inside the membrane against the solution outside is equal to the sum of the osmotic pressure of the colloidal particles, and the difference in the osmotic pressures of the ions inside and outside the membrane. If dissociation is complete and the concentration of the colloidal particles is c ($c=1$ when the number of colloidal particles per litre = Avogadro's constant), the osmotic pressure becomes

$$P = RT(c+w+y-2x). \quad . \quad . \quad . \quad . \quad (9)$$

Supposing that the osmotic pressure of the colloidal particles is small compared with the difference in the osmotic pressures of the electrolyte on both sides of the membrane, formula (9) can be simplified to

$$P = RT(w+y-2x). \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In order to investigate whether my assumption that adsorption of ions on colloidal particles causes such an unequal distribution of an electrolyte, the present research was carried out. For the purpose of freeing the problem from every complication, I had to choose, as a colloid, one that was not a colloidal electrolyte, and as dialysable

electrolyte, one which certainly did not give any chemical reaction with the colloid. I chose as colloid colloidal sulphur, and as dialysable electrolyte HCl. From Odén's * and Freundlich and Scholz's † researches, it is likely that sulphur particles hold ions adsorbed. By means of fractional coagulation it is possible to get fairly uniform sulphur sols, which are stable in rather concentrated acids and therefore could be supposed to be suitable for such a research.

The sulphur sols were prepared according to Raffo's ‡ method from conc. $Na_2S_2O_3$-solution and conc. H_2SO_4. The colloidal sulphur formed was reversibly coagulated by conc. NaCl-solution, and the coagulum, separated from the liquid by centrifuging, was dissolved in lukewarm water. This operation was repeated until the liquid above the coagulum gave a neutral reaction. The sulphur was then dissolved in a large volume of water, so that the sulphur concentration was about 5 gm. per litre, and this sol (the original sol) was divided up into uniform sols by fractional coagulation. To the sulphur sol was added such a quantity of 1-normal NaCl solution that the NaCl concentration in the sol was 0·10 N. The coagulated sulphur was centrifuged off, dissolved in water, and this sol was marked (–0·10). In this way the original sol was divided up into five sols, marked: (–0·10), (0·10–0·20), (0·20–0·30), (0·30–0·40), and (0·40–). These sulphur sols were then repeatedly coagulated with conc. HCl until an analysis showed that they did not contain Na ions.

These sols were rather acid, and I tried to free them from acid by dialysing through collodion bags, which I prepared by pouring very concentrated collodion inside an Erlenmeyer flask and drying the collodion film hard. On the collodion bag was fixed a narrow glass tube which acted as an open manometer, from which the osmotic pressure of the sulphur sol against the liquid outside could be read. The dialysing process was continued during nearly two months, the water outside the membrane being changed every second day. I found that after this time acid still dialysed out from the sulphur sol, but at the same time irreversibly coagulated sulphur was formed. It is therefore probable that sulphur particles which lose all of their adsorbed ions coagulate irreversibly.

I tried at first to determine the hydrogen ion activity with an ordinary hydrogen electrode, but this was impossible, since

* Sven Odén, "Der Kolloide Schwefel," *Nov. act. reg. soc. scient. Upsala*, ser. 4, iii. No. 4 (1913).

† H. Freundlich and P. Scholz, *Koll. Beih.* xvi. p. 234 (1922).

‡ M. Raffo, *Kolloid Zeit.* ii. p. 358 (1908).

the electrode became poisoned from the colloidal sulphur, and the values of the E.M.F. were neither constant nor reproducible. Neither was it possible to determine p_H in the sulphur sols by means of indicators, as they were adsorbed on the colloid and gave a colour to the solution which was not composed of the added colours of the sulphur sol and the indicator. Fortunately, however, I found that Biilmann's quinhydrone electrode could be used for determination of the hydrogen ion activity in sulphur sols.

I have in my experiments used the following three cells :—

1. Quinhydrone electrode, Solution inside the membrane | KCl sat. sol. | Calomel electrode,
2. Quinhydrone electrode, Solution outside the membrane | KCl sat. sol. | Calomel electrode,
3. Calomel electrode | Solution outside the membrane || Solution inside the membrane | Calomel electrode.

Membrane.

Supposing that the E.M.F.'s of these cells are E_i, E_0 and E_m, a_1 and a_2 the hydrogen ion activity inside and outside the membrane, and that

$$p_{a_1} = \log \frac{1}{a_1}, \qquad p_{a_2} = \log \frac{1}{a_2},$$

the following equations are applicable if the saturated calomel electrode is used and the temperature is 18°:

$$E_i - E_0 = E_m \text{ (the membrane potential)}, \quad . \quad (11)$$

$$p_{a_1} = \frac{0{\cdot}4510 - E_i}{0{\cdot}0577}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$p_{a_2} = \frac{0{\cdot}4510 - E_0}{0{\cdot}0577}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The E.M.F.'s of both the first cells increased rapidly during the first half-hour after the cell was built up ; and then became constant or fell slowly. I have in my results used the maximum value of the E.M.F. As a rule, the more acid the solution contained the more constant was the E.M.F. I failed very often in measuring the membrane potential E_m and could find no reason why. When, however, I got a constant value for E_m, it checked well with $E_i - E_0$, as the following tables show. A necessary condition was that during the measurement of E_m the pressure from the solution inside against the solution outside the membrane must be the same as the osmotic pressure at equilibrium.

The experiments were carried out in the following manner. The collodion bag (volume 200 c.c.) and the manometer were filled with a dialysed sulphur sol and put into a three-litre beaker with diluted acid. After about 48 hours the osmotic pressure had become constant, showing that equilibrium was reached. During the time of dialysing, stirring was often accomplished by pressing the walls of the collodion bag together. After 72 hours dialysing, 5 c.c. of the sulphur sol were taken out from the collodion bag by means of a pipette, saturated with quinhydrone, and E_i was measured. In place of the 5 c.c. which were taken out, the collodion bag was refilled with another 5 c.c. pure sol, so that the concentration of sulphur inside the membrane was constant. I have calculated that during one series of experiments with a sol, the sulphur concentration varied less than one per cent. The activity a_2 of the hydrochloric acid outside the membrane was also measured with Biilmann's quinhydrone electrode. The acidity outside the membrane was then increased, and after another three days a new reading was taken. This procedure was continued until the acidity was so high that E_i and E_0 attained the same value within experimental error. Even at this concentration of the acid no coagulation could be traced. The last experiments in the following Tables IV. and V. were made in order to find whether I got the same values for E_i, E_0 and the osmotic pressure when the membrane equilibrium was reached by decreasing the acidity outside the membrane. The values obtained in these cases are, within the experimental error, the same as when the acidity is increased.

For eliminating the liquid junction potential I used a saturated KCl solution. It is obvious that this potential can be neglected, because if there were a liquid junction potential I should never have obtained $E_i - E_0 = 0$, but certain positive or negative values which were equal to the liquid junction potential.

The sulphur concentrations in the sols were determined by oxidation of the sulphur with bromine, and the sulphuric acid was weighed as $BaSO_4$. The sulphur concentrations were :—

0·10–0·20	.....	14·75 gram S per litre.
0·20–0·30	.....	7·99 „ „ „ „
0·30–0·40	.....	29·17 „ „ „ „
0·40–	.....	34·21 „ „ „ „

The sol (–0·10) showed a very small membrane effect, and no measurements were made on this.

Fig. 1.

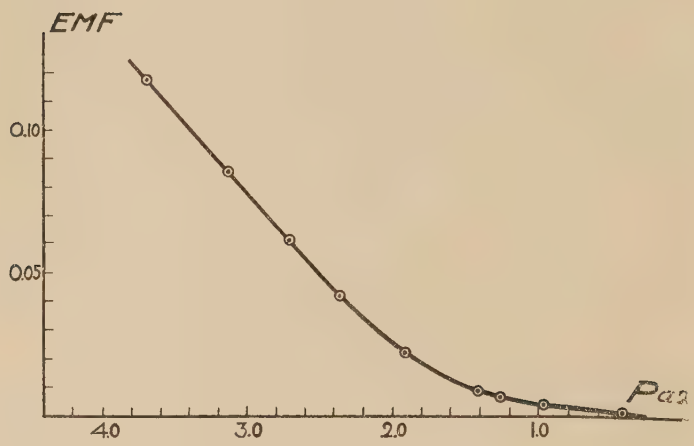
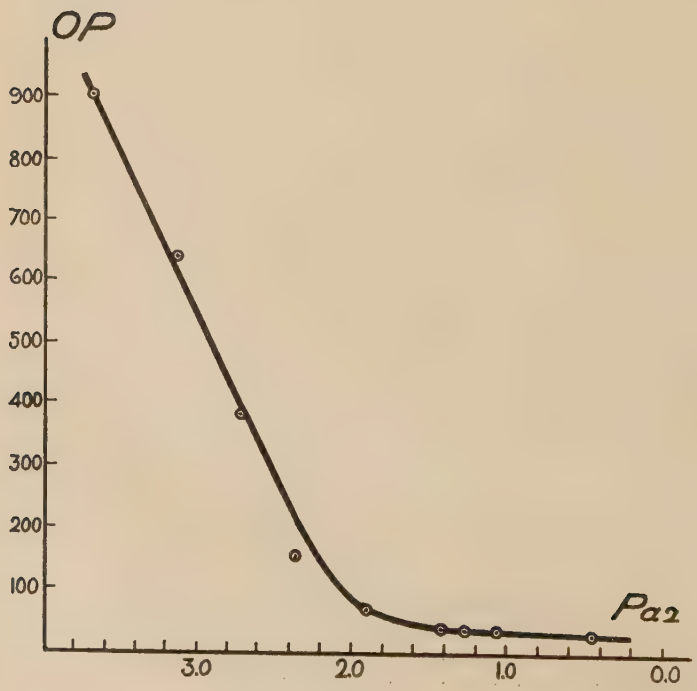

EMF
0.10
0.05
4.0
3.0
2.0
1.0
Pa2

Fig. 2.


OP
900
800
700
600
500
400
300
200
100
3.0
2.0
1.0
0.0
Pa2

The results are reproduced in Tables II.–V., and in figs. 1 and 2 are given the values for the membrane potential ($E.M.F. = E_i - E_0$), and the observed osmotic pressure in mm. H_2O (O.P.) plotted against the negative logarithm of the hydrogen ion activity outside the membrane (p_{a_2}). The numerical values are taken from Table V.

The membrane potential has its highest value when the acidity of the colloid is small, decreasing when the acidity rises and approaching zero.

The curve for the osmotic pressure has the same shape as the membrane potential curve. It is, however, approaching not zero, but a certain positive value. It can be supposed that this pressure is due to the colloidal particles themselves and proceeding from this assumption it would be possible to calculate the size of the sulphur particles. If such a calculation is carried out, one finds that the sol (0·10–0·20) would contain the smallest particles and the sol (0·40–) the largest. An examination of the colloids in the ultramicroscope shows that the sol (0·10–0·20) contains very large particles and the sol (0·40–) only amicrons. The simple assumption that this minimum pressure would be the pressure from the colloidal particles only is therefore incorrect. The column P_{cal} in the tables contains calculated values of the osmotic pressure according to formula (10), in the cases where complete ionization could be supposed. This value is many times larger than the experimentally determined osmotic pressure. A similar relation has been found by E. and H. Hammarsten * in their research concerning the osmotic pressures of certain electrolytes with large molecules. These authors advance a theory according to which a colloidal ion and an ordinary ion act osmotically as one particle when the distance between them is less than a certain value b, and as two particles when this distance is larger than b. This theory is also applicable in the case of the sulphur sols. However, from my experiments I can only draw the conclusion that it is impossible at this time to calculate either the size of the particles or the membrane equilibrium, from the osmotic pressure.

In the tables, S is the concentration of sulphur in grams per litre, and z/S is therefore the concentration of monovalent ions adsorbed on each gram of sulphur. In fig. 3,

* Einar and Harald Hammarsten, *Arkiv för Kemi Mineralogi och Geologi*, Bd. viii. No. 27, p. 1 (1923).

TABLE II.

P.	$P_{cal.}$	E_i.	pa_1.	a_1.	E_0.	pa_2.	a_2.	f.
215	309	0·2855	2·867	$1·36 . 10^{-3}$	0·2055	4·253	$5·58 . 10^{-5}$	1
100	227	0·2877	2·829	1·48 . „	0·2490	3·499	$3·17 . 10^{-4}$	1
24	163	0·3015	2·590	2·57 . „	0·2845	2·884	$1·31 . 10^{-3}$	0·98
20	...	0·3300	2·096	8·02 . „	0·3257	2·171	6·75 . „	0·93

TABLE III.

P.	$P_{cal.}$	E_i.	pa_1.	a_1.	E_0.	pa_2.	a_2.	f.
284	378	0·2897	2·794	$1·61 . 10^{-3}$	0·1997	4·353	$4·44 . 10^{-5}$	1
198	390	0·2954	2·696	2·01 . „	0·2412	3·635	$2·32 . 10^{-4}$	1
120	319	0·2982	2·647	2·25 . „	0·2622	3·263	5·46 . „	
20	...	0·3107	2·375	4·20 . „	0·3010	2·598	$2·52 . 10^{-3}$	0·96
15	...	0·3344	2·020	9·55 . „	0·3303	2·091	8·11 . „	0·93
12	...	0·3683	1·433	$3·69 . 10^{-2}$	0·3667	1·460	$3·47 . 10^{-2}$	0·85
11	...	0·4030	0·8313	$1·48 . 10^{-1}$	0·4028	0·835	$1·46 . 10^{-1}$	0·78

TABLE IV.

P.	$P_{cal.}$	E_i.	pa_1.	a_1.	E_0.	pa_2.	a_2.	f.	$E_i - E_0$.
620	4100	0·3458	1·823	$1·50 . 10^{-2}$	0·2161	4·069	$8·53 . 10^{-5}$	1	0·1297
350	4910	0·3507	1·738	1·83 . „	0·2555	3·309	$4·91 . 10^{-4}$	1	0·0952
272	3970	0·3463	1·814	1·54 . „	0·2767	3·030	9·33 . „	1	0·0696
72	...	0·3490	1·767	1·71 . „	0·3081	2·475	$3·55 . 10^{-3}$	0·95	0·0409
38	...	0·3578	1·615	2·43 . „	0·3378	1·961	$1·09 . 10^{-2}$	0·91	0·0200
37	...	0·3718	1·372	4·25 . „	0·3642	1·504	3·13 . „	0·86	0·0076
35	...	0·4104	0·703	$1·98 . 10^{-1}$	0·4090	0·7276	$1·87 . 10^{-1}$	0·78	0·0014
36	...	0·3788	1·251	$5·61 . 10^{-2}$	0·3727	1·357	$4·40 . 10^{-2}$	0·84	0·0061

(0·10–0·20.)

$E_i - E_0$.	a_1/a_2.	a_2/a_1.	$[H_1]$.	$[Cl_1]$.	$[H_2]$.	z.	z/S.
0·0800	24·3	0·04	$1·36 . 10^{-3}$	$2·29 . 10^{-6}$	$5·58 . 10^{-5}$	$1·36 . 10^{-3}$	$0·92 . 10^{-4}$
0·0387	4·68	0·21	$1·48 . 10^{-3}$	$0·68 . 10^{-4}$	$3·17 . 10^{-4}$	$1·41 . 10^{-3}$	$0·96 . 10^{-4}$
0·0170	1·97	0·51	$2·65 . 10^{-3}$	$6·90 . 10^{-4}$	$1·34 . 10^{-3}$	$1·96 . 10^{-3}$	$1·33 . 10^{-4}$
0·0043	1·19	0·84	$8·63 . 10^{-3}$	$6·11 . 10^{-3}$	$7·25 . 10^{-3}$	$2·55 . 10^{-3}$	$1·73 . 10^{-4}$

(0·20–0·30.)

$E_i - E_0$.	a_1/a_2.	a_2/a_1.	$[H_1]$.	$[Cl_1]$.	$[H_2]$.	z.	z/S.
0·0900	36·2	0·03	$1·61 . 10^{-3}$	$1·22 . 10^{-6}$	$4·44 . 10^{-5}$	$1·61 . 10^{-3}$	$2·01 . 10^{-4}$
0·0542	8·69	0·12	$2·01 . 10^{-3}$	$2·68 . 10^{-5}$	$2·32 . 10^{-4}$	$1·98 . 10^{-3}$	$2·48 . 10^{-4}$
0·0360	4·13	0·24	$2·25 . 10^{-3}$	$1·33 . 10^{-4}$	$5·46 . 10^{-4}$	$2·12 . 10^{-3}$	$2·66 . 10^{-4}$
0·0097	1·67	0·60	$4·38 . 10^{-3}$	$1·57 . 10^{-3}$	$2·63 . 10^{-3}$	$2·81 . 10^{-3}$	$3·52 . 10^{-4}$
0·0041	1·18	0·85	$1·03 . 10^{-2}$	$7·43 . 10^{-3}$	$8·74 . 10^{-3}$	$2·88 . 10^{-3}$	$3·62 . 10^{-4}$
0·0016	1·06	0·94	$4·35 . 10^{-3}$	$3·86 . 10^{-2}$	$4·08 . 10^{-2}$	$4·90 . 10^{-3}$	$6·14 . 10^{-4}$
0·0002	1·01	0·99	$1·90 . 10^{-1}$	$1·86 . 10^{-1}$	$1·85 . 10^{-1}$	$3·70 . 10^{-2}$	$4·55 . 10^{-3}$

(0·30–0·40.)

E_m.	a_1/a_2.	a_2/a_1.	$[H_1]$.	$[Cl_1]$.	$[H_2]$.	z.	z/S.
0·1298	176	0·006	$1·50 . 10^{-2}$	$5 . 10^{-6}$	$8·53 . 10^{-5}$	$1·50 . 10^{-2}$	$5·15 . 10^{-4}$
0·0922	37·2	0·03	$1·83 . 10^{-2}$	$1·3 . 10^{-5}$	$4·91 . 10^{-4}$	$1·83 . 10^{-2}$	$6·30 . 10^{-4}$
0·0702	16·4	0·06	$1·54 . 10^{-2}$	$5·7 . 10^{-5}$	$9·33 . 10^{-4}$	$1·54 . 10^{-2}$	$5·28 . 10^{-4}$
...	5·11	0·20	$1·80 . 10^{-2}$	$0·7 . 10^{-3}$	$3·74 . 10^{-3}$	$1·73 . 10^{-2}$	$5·93 . 10^{-4}$
...	2·22	0·45	$2·67 . 10^{-2}$	$5·4 . 10^{-4}$	$1·20 . 10^{-2}$	$2·13 . 10^{-2}$	$7·30 . 10^{-4}$
...	1·36	0·74	$4·95 . 10^{-2}$	$2·68 . 10^{-2}$	$3·62 . 10^{-2}$	$2·25 . 10^{-2}$	$7·75 . 10^{-4}$
...	1·06	0·94	$2·54 . 10^{-1}$	$2·26 . 10^{-1}$	$2·40 . 10^{-1}$	$2·89 . 10^{-2}$	$9·94 . 10^{-3}$
...	1·28	0·78	$6·69 . 10^{-2}$	$4·07 . 10^{-2}$	$5·24 . 10^{-2}$	$2·62 . 10^{-2}$	$8·98 . 10^{-3}$

TABLE V.

P.	P	E_i.	pa_1.	a_1.	E_0.	pa_2.	a_2.	f.	$E_i - E_0$.	E_m.
905	5220	0·3548	1·667	$2·15 . 10^{-2}$	0·2375	3·700	$2·00 . 10^{-4}$	1	0·1173	0·1173
640	5500	0·3555	1·654	2·22 . „	0·2703	3·130	7·41 . „	1	0·0852	...
383	5450	0·3548	1·667	2·15 . „	0·2940	2·720	$1·91 . 10^{-3}$	0·98	0·0608	0·0695
154	...	0·3560	1·646	2·26 . „	0·3143	2·268	4·29 . „	0·95	0·0414	...
71	...	0·3626	1·531	2·94 . „	0·3410	1·905	$1·25 . 10^{-2}$	0·90	0·0216	0·0220
43	...	0·3778	1·268	5·40 . „	0·3697	1·408	3·91 . „	0·85	0·0081	0·0085
38	...	0·3981	0·916	$1·21 . 10^{-1}$	0·3948	0·974	$1·06 . 10^{-1}$	0·80	0·0032	...
35	...	0·4265	0·424	3·77 . „	0·4255	0·442	3·62 . „	0·76	0·0010	0·0007
42	...	0·3838	1·164	$6·86 . 10^{-2}$	0·3775	1·273	$5·33 . 10^{-2}$	0·83	0·0063	...

TABLE VI. (Loeb:

$$z_1 = \frac{a_2}{f}\left[\frac{a_2}{a_1} - \frac{a_1}{a_2}\right];$$

pa_1 = "p_H inside."	pa_2 = "p_H outside."	$pa_1 - pa_2$.	a_1.	a_2.	f.	a_2/a_1.	a_1/a_2.
4·56	4·14	0·42	$2·75 . 10^{-5}$	$7·24 . 10^{-5}$	1	2·63	0·38
4·31	3·78	0·53	4·90 . „	$1·66 . 10^{-4}$	1	3·39	0·30
4·03	3·44	0·59	9·33 . „	3·63 . „	1	3·89	0·26
3·85	3·26	0·59	$1·41 . 10^{-4}$	5·50 . „	0·99	3·89	0·26
3·33	2·87	0·46	4·68 . „	$1·35 . 10^{-3}$	0·98	2·88	0·34
3·25	2·81	0·44	5·62 . „	1·55 . „	0·97	2·75	0·35
2·85	2·53	0·32	$1·41 . 10^{-3}$	2·95 . „	0·96	2·09	0·48
2·52	2·28	0·24	3·02 . „	5·25 . „	0·94	1·74	0·58
2·13	2·00	0·13	7·41 . „	$1·00 . 10^{-2}$	0·92	1·35	0·74
1·99	1·89	0·10	$1·02 . 10^{-2}$	1·29 . „	0·90	1·26	0·79
1·79	1·72	0·07	1·62 . „	1·86 . „	0·88	1·17	0·85
1·57	1·53	0·04	2·68 . „	2·96 . „	0·86	1·10	0·90

(0·40– .)

a_1/a_2.	a_2/a_1.	$[H_1]$.	$[Cl_1]$.	$[H_2]$.	z.	z/S.	z_a.
108	0·009	$2·15 . 10^{-2}$	$2·0 . 10^{-6}$	$2·0 . 10^{-4}$	$2·15 . 10^{-2}$	$6·28 . 10^{-4}$	...
29·9	0 03	2·22. „	$2·5 . 10^{-5}$	$7·41 . 10^{-4}$	2·22. „	6·50. „	$2·15 . 10^{-2}$
11·3	0·09	2·20. „	$1·7 . 10^{-4}$	$1·95 . 10^{-3}$	2·20. „	6·45. „	2·17. „
5·27	0·19	2·38. „	$0·09 . 10^{-2}$	$4·52 . 10^{-3}$	2·29. „	6·70. „	2·27. „
2·35	0·42	3·27. „	0·60. „	$1·39 . 10^{-2}$	2·68. „	7·85. „	2·67. „
1·38	0·72	6·36. „	3·33. „	4·60. „	3·03. „	8·85. „	3·21. „
1·14	0·88	$1·51 . 10^{-1}$	$1·16 . 10^{-1}$	$1·33 . 10^{-1}$	3·56. „	10·10. „	3·40. „
1·04	0·96	4·96. „	4·58. „	4·76. „	3·82. „	11·15. „	3·48. „
1·29	0·78	$8·28 . 10^{-2}$	$5·00 . 10^{-2}$	$6·42 . 10^{-2}$	3·28. „	9·59. „	3·29. „

Proteins, etc., p. 128, table xi.)

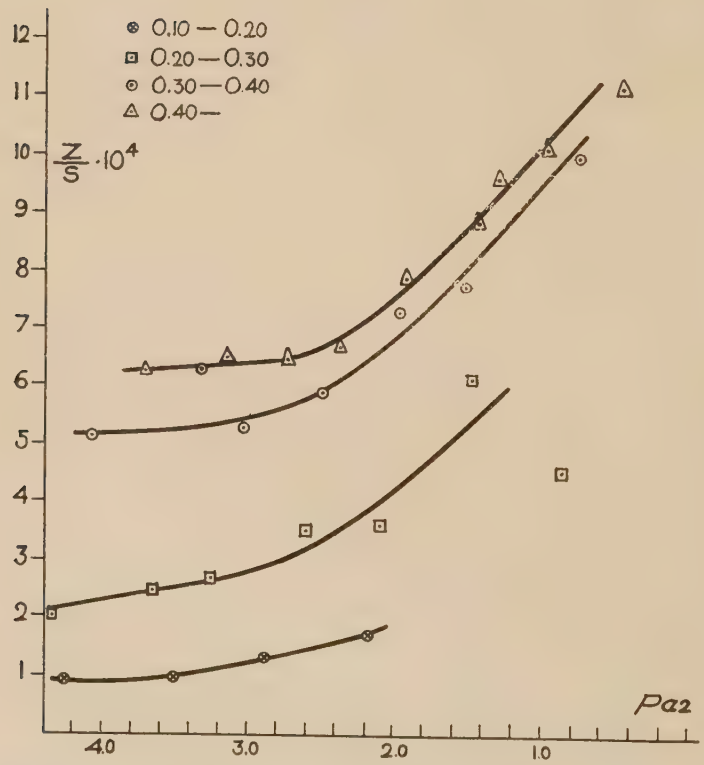
$$z_2 = \frac{14·6 \,.\, a_1/f}{1 + 2100 \,.\, a_1/f}.$$

a_1/f.	a_2/f.	z_1.	a_1/fz_1.	z_2.	$z_2 - z_1$.
$2·75 . 10^{-5}$	$7·24 . 10^{-5}$	$0·16 . 10^{-3}$	$1·72 . 10^{-1}$	$0·26 . 10^{-3}$	$+0·10 . 10^{-3}$
$4·90 . 10^{-5}$	$1·66 . 10^{-4}$	$0·51 . 10^{-3}$	$9·6 . 10^{-2}$	$0·65 . 10^{-3}$	$+0·14 . 10^{-3}$
$9·33 . 10^{-5}$	$3·63 . 10^{-4}$	$1·32 . 10^{-3}$	$7·1 . 10^{-2}$	$1·30 . 10^{-3}$	$-0·02 . 10^{-3}$
$1·43 . 10^{-4}$	$5·55 . 10^{-4}$	$2·00 . 10^{-3}$	$7·0 . 10^{-2}$	$1·61 . 10^{-3}$	$-0·39 . 10^{-3}$
$4·80 . 10^{-4}$	$1·38 . 10^{-3}$	$3·50 . 10^{-3}$	$1·37 . 10^{-1}$	$3·50 . 10^{-3}$	...
$5·85 . 10^{-4}$	$1·60 . 10^{-3}$	$3·84 . 10^{-3}$	$1·52 . 10^{-1}$	$3·86 . 10^{-3}$	$+0·02 . 10^{-3}$
$1·47 . 10^{-3}$	$3·07 . 10^{-3}$	$4·95 . 10^{-3}$	$2·97 . 10^{-1}$	$5·25 . 10^{-3}$	$+0·30 . 10^{-3}$
$3·22 . 10^{-3}$	$5·59 . 10^{-3}$	$6·48 . 10^{-3}$	$4·96 . 10^{-1}$	$6·10 . 10^{-3}$	$-0·38 . 10^{-3}$
$8·15 . 10^{-3}$	$1·09 . 10^{-2}$	$6·63 . 10^{-3}$	1·23	$6·60 . 10^{-3}$	$-0·03 . 10^{-3}$
$1·12 . 10^{-2}$	$1·44 . 10^{-2}$	$6·77 . 10^{-3}$	1·66	$6·70 . 10^{-3}$	$-0·07 . 10^{-3}$
$1·81 . 10^{-2}$	$2·12 . 10^{-2}$	$6·80 . 10^{-3}$	2·66	$6·80 . 10^{-3}$	...
$3·13 . 10^{-2}$	$3·45 . 10^{-2}$	$6·90 . 10^{-3}$	4·55	$6·86 . 10^{-3}$	$-0·05 . 10^{-3}$

z/S is plotted against p_{a_2}. As the figure shows, the quantity of adsorbed ions is fairly constant when the acidity outside the membrane is low, and rises when the acidity increases. A qualitative analysis of the dialysed sulphur sol gave no reaction for chlorine. The ions adsorbed in such a sol may therefore be those of some other acid, and the concentration of this is :

0·09 millimol per gram sulphur for the sol								0·10–0·20
0·2	„	„	„	„	„	„	„	0·20–0·30
0·5	„	„	„	„	„	„	„	0·30–0·40
0·6	„	„	„	„	„	„	„	0·40–

Fig. 3.



From their investigations, Freundlich and Scholtz * have drawn the conclusion that the stability of the sulphur sols depends upon adsorbed pentathionic acid, and that the

* *L. c.*

quantity of adsorbed acid in a Raffo sol is 0·47–0·69 millimol per gram sulphur. My experiments confirm such an assumption.

When, however, the hydrochloric acid concentration rises, chlorine ions become adsorbed. Langmuir has in some of his papers suggested a theory of adsorption *. Gustaver † has successfully used this theory in investigating the adsorption of picric acid by charcoal. Langmuir assumes in his theory that on the surface of the adsorbing substance there are a certain number of elementary spaces, where there are residual valencies. If Langmuir's theory is applicable to the adsorption of ions on colloidal particles, we may write

$$z = \frac{k_1 c}{1 + k_2 c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where z is the concentration of adsorbed ions, c the concentration of the same ions in the solution, and k_1 and k_2 are constants. I have tried to apply this formula to the results reproduced in Table V. The adsorbed ions are partly chlorine ions and partly ions of another acid, possibly pentathionic acid ; and if the concentration of this is equal to z in the first experiment in Table V. ($=2{\cdot}15 \,.\, 10^{-2}$), the other values of z may be expressed by :

$$z_a = 2{\cdot}15 \,.\, 10^{-2} + \frac{1{\cdot}5 \, Cl_1}{1 + 111 \, Cl_1}. \quad . \quad . \quad . \quad (15)$$

The results obtained by calculating according to this formula are reproduced in column z_a, Table V. The agreement between z and z_a is fairly good.

As an analysis shows, there are also neutral HCl molecules adsorbed on the sulphur particles. I have, however, not determined their amount, as it was of little importance for this research, and as the time I had at my disposal was very short. I will at least point out that I have in my experiments been rather far from the point of reversible coagulation. For instance, in Table V. I have not been able to measure the adsorption of ions beyond an acidity of 0·5 N, and for this sol the reversible coagulation sets in at an acidity of about 5 N. This method gives therefore no information concerning the variation in ionic adsorption when the acidity varies between 0·5 and 5 normal.

* I. Langmuir, Journ. Amer. Chem. Soc. xxxviii. (1916); xxxix. (1917); xl. (1917).

† B. Gustaver, *Kollidchem. Beih.* xv. (1922).

J. Loeb has, in his monograph "Proteins and the Theory of Colloidal Behaviour," given an account of his experiments on gelatine. He thinks he has proved that gelatine gives a real chemical reaction with acids or bases. His point of view can doubtless be best expressed by his own words, taken from the preface of his book :—

"Colloid Chemistry has been developed on the assumption that the ultimate unit in colloidal solutions is not the isolated molecule or ion but an aggregate of molecules or ions, the so-called micella of Naegeli. Since it seemed improbable that aggregates could combine in stoichiometrical proportions with acids, alkalies, or salts, the conclusion was drawn that electrolytes were adsorbed on the surface of colloidal particles according to a purely empirical formula, Freundlich's adsorption formula. The writer's investigations have led to the result that this last conclusion is based on a methodical error, as far as the proteins are concerned. . . . . It is found that proteins combine with acids and alkalies according to the stoichiometrical laws of the classical chemistry and that the chemistry of proteins does not differ from the chemistry of crystalloids."

Loeb has, among other things, measured the membrane potential and the osmotic pressure, and the curves obtained when the membrane potential and the osmotic pressure are plotted arainst the values of p_H are of a different type from those I have obtained for colloidal sulphur. By adding HCl to gelatine and starting from the isoelectric point, the E.M.F. and O.P. increase, pass through a maximum, and then decrease. It may be of some interest to see how the concentration of the nondialysable ions varies with the acidity. It is possible to calculate this for HCl according to formula (7). For H_2SO_4, H_3PO_4, etc., this formula is not applicable, because the approximations made in its deduction are not allowable for these acids. The experimental values are taken from Loeb's monograph, p. 128, table xi., and reproduced in Table VI. in this paper. In this table p_{a_1} and p_{a_2} are written instead of Loeb's values, "p_H inside" and "p_H outside." The other letters in the table have the same meaning as in the preceding tables in this paper.

I have, however, tried to apply Langmuir's adsorption theory to the case of gelatine by making a theoretical calculation of the z values. In this case there would be an adsorption of hydrogen ions, and the adsorption formula would be

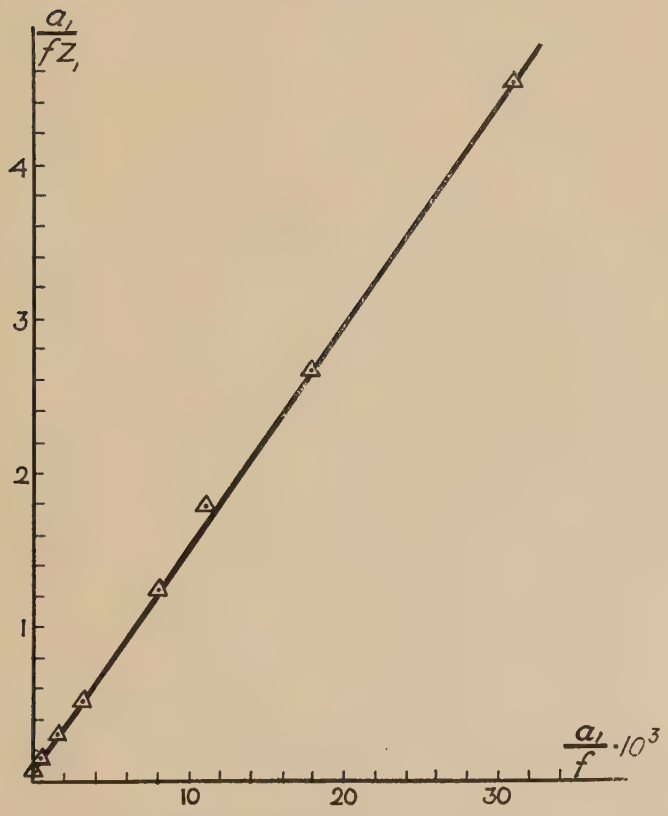
$$z = \frac{k_1 a_1 / f}{1 + k_2 a_1 / f}, \quad \ldots\ldots \quad (16)$$

or transformed,

$$\frac{a_1}{fz} = \frac{k_2}{k_1}\frac{a_1}{f} + \frac{1}{k_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If a_1/fz is plotted against a_1/f it is obvious from equation (17) that all the points would lie on a straight line if Langmuir's adsorption formula were applicable. This is done in fig. 4,

Fig. 4.



and, as the figure shows, this is the case. If the constants k_1 and k_2 are calculated from this straight line, the formula (16) can be written:

$$z_2 = \frac{14{\cdot}6 \,.\, a_1/f}{1 + 2100\, a_1/f} \quad . \quad , \quad . \quad . \quad . \quad (18)$$

From the columns z_2 and $z_2 - z_1$ in Table VI. it is evident

that the theoretical values for the amount of adsorbed ions and the values calculated from determinations of the activities inside and outside the membrane check surprisingly well, and it is therefore very likely that the "reaction" between gelatine and HCl is not a chemical reaction in the sense assumed by Loeb, but an adsorption process, and that the hydrogen ions are bound by means of residual valencies to the gelatine particles. Exceptions from this may occur in the region of the isoelectric point, where a real chemical reaction may take place. Besides this adsorption of hydrogen ions there is also an adsorption of neutral HCl molecules, as can be calculated from Loeb's experimental results. A closer criticism of Loeb's work is, however, outside the scope of this paper.

In a recent paper (*Zeitschrift für Physikalische Chemie*, cx. p. 656, 1924) N. Bjerrum has published a research entitled: "Zur Theorie der osmotischen Drucke, der Membranpotentiale und der Ausflockung von Kolloiden." In this paper he has shown that colloidal chromium hydroxide gives a membrane equilibrium effect. He supposes that this is due to the fact that colloidal chromium hydroxide is to be considered as a high molecular, multivalent, strong electrolyte. Unfortunately there are in this paper a number of errors, and I will here call attention to only a few of them.

The particles in the colloid are positively charged, q is the average number of positive charges per chromium atom, $[Cr]$ the number of chromium atoms per litre, p the amount of adsorbed anions per chromium atom, and on p. 677 he writes: "Fügt man zu p, die Zahl der adsorbierten Anionen, q, die Zahl der freien Ladungen, so erhält man die Gesamtladung der Kolloidpartikeln pro Cromatom." In table 8 (p. 676) is a column with the sum (not algebraical) of $p+q$. A sum of positive and negative charges cannot, however, be an expression for the charge of colloidal particles. Upon closer consideration of Bjerrum's experimental results, one finds that p is about 10 times as large as q. According to this the particle would be negatively charged, a conclusion which is opposed to his experimental results. From his method of determining p it is, however, evident that p is the quantity of adsorbed chromium chloride or hydrochloric acid molecules. $q[Cr]$ signifies the quantity designated by z in the preceding part of this paper, and is therefore the concentration of adsorbed cations (chromium ions?).

Bjerrum supposes further that q is a constant. As he has not kept the chromium concentration constant it is impossible, according to equation (7), to calculate q values which can be

compared with each other. In Bjerrum's paper, p. 663, table 1, three experiments made the 28th October, the 5th November, and the 20th November, 1919, are, however, described, where the chromium concentration is constant ([Cr] = 0·051) and the acidity varies. The results are assembled in Table VII.

Table VII.

a_2/f.	E_m.	a_2/a_1.	a_1/a_2.	$z=q[Cr]$.	q.
0·005	0·0091	1·44	0·70	0·0037	0·073
0·0025	0·0161	1·90	0·53	0·0034	0·067
0·001	0·0282	3·08	0·32	0·0028	0·055

From this table it is obvious that the amount of adsorbed cations increases with the acidity and q is not to be considered as a constant. All the conclusions which Bjerrum has drawn from this assumption—for instance, that the number of chromium atoms per chromium hydroxide particle is 1000, etc.—must therefore be wrong. On p. 672, table 6, Bjerrum has calculated the values of q, but these are only about half as large as those given in Table VII. I think that this depends, among other things, upon the fact that Bjerrum has used the osmotic pressure for the calculation of q, which is not permissible for these large particles according to Hammarsten's and this research. In closing, I will only correct a mathematical error. In Bjerrum's paper

$$x = \frac{E_m F}{RT} \quad \text{and} \quad P_2 = RT\,cx^2 \quad \text{(formula 13)}.$$

The formula (22) should therefore be

$$P_2 = \frac{F^2}{RT} E_m{}^2 c,$$

and thus formula (23)

$$E_m = \text{const.} \sqrt{\frac{P_2}{c}}$$

instead of Bjerrum's formula. I have not calculated the constant as the formula is of very little importance, partly because, as already stated, the osmotic pressure cannot be

used for such calculations, and partly because the cases where the series development can be broken off at the first term, as Bjerrum has done, should be considered as exceptions.

The present investigation was carried out with the assistance of a stipendium from C. F. Liljewalch's Stipendium Fund of the University of Upsala.

I desire to take this opportunity of expressing my indebtedness to Prof. F. G. Donnan for his kindly interest and helpful criticism. I also wish to thank Prof. A. V. Hill for his kindness in allowing me to use one of his centrifuges.

The Sir William Ramsay Laboratories of
Inorganic and Physical Chemistry,
University College, London.
November 1924.

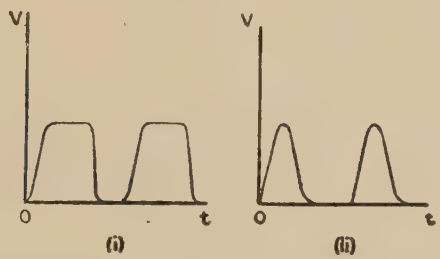
IV. *The Distribution of Energy in the Continuous X-ray Spectrum.* *By* MAURICE H. BELZ, *M.Sc., Lecturer in Mathematics in the University of Melbourne* *.

THE accurate knowledge of the distribution of the energy emitted from an X-ray bulb under any given form of potential and current is of signal importance in all applications of the rays. If it were possible simply and quickly to predict the nature of the distribution of the energy from a knowledge of the variations of potential and current, it might be anticipated that a standardization of methods would be possible, especially in regard to applications to therapy. I is now well known that an X-ray tube, for example a standard Coolidge tube, will emit rays of different quality depending on the form of the applied potential. If a comparison be made between the energy wave-length curves for different types of voltage, it is found that for equality of maximum potential and mean current the curves are considerably different. The maximum energy is emitted for different wave-lengths, and the measure of this maximum energy is different for each case. This fact seems not only to rob the modern practice of deep therapy X-ray treatment of a scientific basis, but also to give to it a suggestion of chance. In particular, the treatment for a certain disease may be expressed as a dose of a certain potential and a certain

* Communicated by Prof. T. H. Laby, M.A., Sc.D., F.Inst.P.

current acting for a specified time. This time is governed in the first place by the erythema dose, and the treatment may be thus expressed as equivalent to a certain number of such doses either simultaneously through several ports of entry or repeatedly through one port, sufficient time being allowed to elapse between doses to prevent the occurrence of an erythema. However, this treatment will be different for each machine used. The erythema dose is not only a function of the applied maximum potential and the current through the tube, but most particularly a function of the forms of the potential and current waves. The erythema dose thus depends entirely on the manner of the distribution, with wave-length, of the energy radiated from the tube. In the case of a Coolidge tube, where during the application of the potential the current may be regarded as approximately constant *, if we compare the radiation produced by a potential wave of the form (i), fig. 1, with that produced by a potential wave of the form (ii), then allowing equivalence

Fig. 1.



of maximum potential, current, and frequency, we can assert that the radiation in the first case will have a maximum energy for a shorter wave-length than in the second case, and, further, that the value of this maximum will be greater in the first case than in the second. Thus the erythema dose may be altogether different in the two cases, and consequently there can be no uniformity of treatment. If, however, X-ray therapy is based on the physical characteristics of the radiation, that is to say, if the dose is expressed in terms of a maximum energy at a given wave-length acting for a given time, a real standardization of treatment may be hoped for. The practitioner would then

* The oscillograph records of the current wave obtained by Crowther (Camb. Phil. Soc. Proc. xxii. p. 70, 1924) in the case of a transformer justify this approximation.

only require to fulfil these conditions for successful treatment, and successful treatment of diseases for which deep therapy is prescribed must be a distinct step forward. Recent improvements in the physical basis of X-ray treatment have been rewarded to such an extent by better results as to encourage further efforts.

The only direct procedure to determine the energy distribution in the radiation from an X-ray bulb is by the employment of an X-ray spectrometer. To conduct such a determination is not only a tedious and difficult task for a medical man, but in most cases would be quite impossible owing to limitations of time and space. It is the object of this paper to point a way to the determination of the energy distribution curve, having given the oscillograph form of the applied potential. The necessary observations upon which any theory may be based are only available for a standard Coolidge X-ray tube, and this tube is the one most commonly employed in applications of X-rays. It will be shown that other types of tubes may be similarly considered, provided that sufficient is known experimentally of their performances.

The commencement of any such determination of the energy wave-length distribution must be made by considering the radiation emitted from the tube when the electrons all have the same speed, that is by considering the case of a constant potential. We may then proceed in two ways. First, we may examine theoretically the relation of the change of kinetic energy of the electron to energy of radiation. Any such treatment involves a number of assumptions, and consequently may be expected to be only an approximation. Theoretical calculations have been made by March *, Davis †, Brillouin ‡, Behnken § and others, but Kirkpatrick ‖ has shown that the theoretical curves only fit the experimental curves very roughly, and accordingly cannot be used as a basis for prediction.

The second method of procedure will thus be from a study of the observed curves for different constant voltages, which have been made to represent the energy distribution of the radiation emitted from the anticathode by the application of a number of corrections. While many observers have examined the distribution from a Coolidge tube with a

* March, *Phys. Zeit.* xxii. pp. 209, 429 (1921).

† Davis, Phys. Rev. ix. p. 64 (1917).

‡ Brillouin, *Comptes Rendus*, clxx. p. 274 (1920).

§ *Zeit. f. Techn. Physik*, vii. p. 153 (1921); and *Zeit. f. Physik*, Bd. iv. p. 241 (1921).

‖ Kirkpatrick, Phys. Rev. xxii. p. 37 (1923).

tungsten anticathode, it is a matter for regret that only two * have carried out these corrections, and as the results of these two observers are not the same, a definite conclusion cannot be arrived at from a study of their curves. The first systematic attempt to coordinate the observations from a Coolidge tube was made by Dauvillier †, who found that under different constant voltages and currents the energy distribution curves satisfied certain definite conditions. While Kirkpatrick ‡ disagrees with one of these conditions, he makes no attempt at definiteness and does not examine any of the other conditions. For this reason Dauvillier's curves have been chosen as a basis for calculation.

Dauvillier's Experimental Curves.

The principal deductions made by Dauvillier from his curves are as follows :—

(i.) Corresponding to any given voltage V, the shortest wave-length at which energy is radiated is given by the relation

$$\lambda_0 = \frac{ch}{eV},$$

where c is the velocity of light, 3×10^{10} cm./sec., h is Planck's constant, $6{\cdot}555 \times 10^{-27}$ ergs, and e is the charge on the electron, $4{\cdot}774 \times 10^{-10}$ e.s.u. If V is expressed in kilovolts, the shortest wave-length, λ_0, expressed in Ångström units, is given practically by the relation

$$\lambda_0 = \frac{12{\cdot}348}{V}.$$

This relation had been proved experimentally by a number of independent observers §.

(ii.) The maximum energy is radiated at a wave-length λ_m given by

$$\lambda_m = 1{\cdot}3\,\lambda_0,$$

provided that λ_0 is less than 0·3 Å.U. (p. 113) ‖.

* Dauvillier, *Ann. de Physique*, xiii. p. 49 (1920), and Kirkpatrick, *loc. cit.*

† Dauvillier, *loc. cit.*

‡ Kirkpatrick, *loc. cit.*

§ See de Broglie, *Les Rayons*, x. p. 77 (1922).

‖ (p. 113) and similar references give the pages in Dauvillier's paper (*loc. cit.*) where the experimental information is recorded.

This law corresponds to Wien's displacement law for the radiation from a black body. For $\lambda_0 > 0{\cdot}3$ Å.U. $\lambda_m > 1{\cdot}3\,\lambda_0$, giving for $\lambda_0 = 0{\cdot}4$ Å.U. $\lambda_m = 1{\cdot}5\,\lambda_0$ approximately.

(iii.) For equal currents through the tube, the maximum energy radiated for different constant potentials is proportional to the square of the potential (p. 115).

(iv.) For equal currents through the tube, the total energy radiated, that is, the area of the distribution curve, for different constant potentials is proportional to the square of the potential (p. 115).

(v.) For equal potentials and different currents through the tube, the minimum energy in each case is radiated at the wave-length given by $\lambda_m = 1{\cdot}3\,\lambda_0$, but the ordinates and areas of the curves are directly proportional to the intensities of the currents in each case (p. 120).

It is possible to find an empirical expression to represent the distribution curve. The conditions to be fulfilled by any such expression may, from Dauvillier's conclusions, be stated briefly thus:—

If E represents the energy radiated between the wave-lengths λ and $\lambda + d\lambda$, then

(i.) $E = 0$ for $\lambda = \lambda_0 = \dfrac{12{\cdot}348}{V}$ Å·U.

(ii.) The maximum energy E_m occurs at $\lambda_m = 1{\cdot}3\,\lambda_0$, if $\lambda_0 < 0{\cdot}3$ Å.U.

(iii.) $E_m = kV^2$, where k is a constant, provided the current is constant.

(iv.) The area of the curve, A, is given by $A = k'V^2$, where k' is a constant, provided the current is constant.

(v.) E, the energy at any wave-length, and A, the area of the curve, are both proportional to i, where i is the current through the tube.

Empirical Law of Distribution.

It is a simplification in the treatment to write $x = \dfrac{\lambda - \lambda_0}{\lambda_0}$ and to consider the graphs wherein energy is plotted against x. The curves given by Dauvillier for voltages 71 kilovolt and 53·5 kilovolt and equal currents, $0{\cdot}5 \times 10^{-3}$ amp., have been redrawn to this new scale and are represented by the curves A and B, fig. 2. In this figure the scale of ordinates is arbitrary. If we denote energy by y,

then if $y = f(x)$ is the empirical relation between y and x, we must have the following conditions :—

(i.) $y = 0$ for $x = 0$.

(ii.) $dy/dx = 0$ for $x = h$, where $h = 0{\cdot}3$, giving a maximum value of y.

(iii.) $y_{\max.} = f(h) = k\mathrm{V}^2$.

(iv.) $\int_0^\infty y \, . \, dx = k_1\mathrm{V}^3$.

(v.) The dependence of y on the current can be expressed by a further relation of the form $y = i \, . f(x)$, where i is the current through the tube. If we can thus find the form of $f(x)$ for any given current, the values of y for any other current can be found by multiplying by an appropriate factor. In the following, the experimental curves for a current 0·5 milliamp. have been employed as the basis of empirical calculations.

The analogy of the distribution curve for X-radiation to that for black body radiation suggested in the first place functions of the type governing the latter radiation. However, all such functions are ineffective on account of their failure to satisfy condition (i.) or difficulty in satisfying condition (iv.). It was thus decided to investigate some similar types of functions which would easily satisfy the conditions. A complete investigation was made of the function

$$y = (ax + bx^2 + cx^3) \, . \, e^{-px},$$

which can be made to satisfy all the conditions. It was unfortunate that the constants of the curve, as determined by the conditions, gave two maxima and a minimum, whereas for slightly different values the curve only had one maximum.

Finally, the following function was examined and found to fit the experimental curves quite well.

We take

$$y = a(e^{-bx} - e^{-cx}).$$

This vanishes for $x = 0$.

Further,

$$dy/dx = a(-be^{-bx} + ce^{-cx})$$

and this has to vanish for $x = h$, giving

$$be^{-bh} - ce^{-ch} = 0.$$

For this value of x the maximum value of y is

$$y_m = a(e^{-bh} - e^{-ch}) = k\mathrm{V}^2 = \mathrm{E}_m \text{ , say,}$$

where E_m is the maximum arbitrary ordinate of any of the

curves. Finally,

$$\int_0^\infty y\,dx = \int_0^\infty a(e^{-bx} - e^{-cx})\,dx$$
$$= a(1/b - 1/c)$$
$$= k_1 V^3 = A, \text{ say,}$$

where A is the arbitrary area of any of the curves.

We thus have the following equations :—

$$be^{-bh} - ce^{-ch} = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$ae^{-bh} - ae^{-ch} = E_m, \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$a/b - a/c = A. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From these we obtain

$$\frac{e^{bh}}{b} = \frac{e^{ch}}{c} = \frac{A}{E_m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and a follows from (2).

Let us now apply this to curve A, fig. 2, for which $h = 0{\cdot}3$, $E_m = 12{\cdot}54$, $A = 28\,71$ *, $V = 71$ kv., and $i = 0{\cdot}5$ milliamp. We have $A/E_m = 2{\cdot}29$.

To find the values of b and c as given by (4), it is most convenient to plot the curve $y = \frac{e^{0{\cdot}3x}}{x}$, and obtain the values graphically. In this case we find $b = 0{\cdot}51$, and $c = 10{\cdot}65$ approximately, the choice of b and c being such as to keep y positive for $x > 0$, which choice also gives $d^2y/dx^2 < 0$ for $x = h$.

With these values of b and c we find, from (2),

$$a = 15{\cdot}35.$$

Hence, we have

$$y = 15{\cdot}35(e^{-0{\cdot}51x} - e^{-10{\cdot}65x}) \quad . \quad . \quad . \quad . \quad (5)$$

as the required relation.

In Table I. the results obtained from the empirical formula (5) and the experimental results are compared.

The curve obtained by means of the relation (5) is shown in fig. 2 by the curve A′.

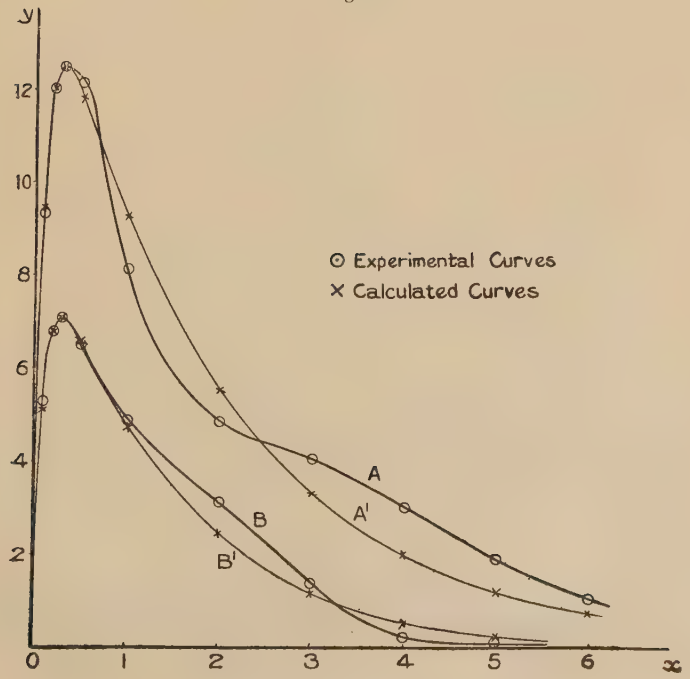
The fit of the two curves, A and A′, is extremely good up to $x = 0{\cdot}7$, and the subsequent departures are probably not greater than the experimental errors. It is difficult to

* The areas given are those of the modified experimental curves which have been continued to become asymptotic to the X-axis.

TABLE I.

x.	y. calculated from (5).	y observed.
0·1	9·3	9·2
0·2	12·0	12·0
0·3	12·54	12·54
0·5	11·8	12·15
1·0	9·22	8·1
2·0	5·55	4·8
3·0	3·34	4·0
4·0	2·0	3·0
5·0	1·2	1·9
6·0	0·72	1·0

Fig. 2.



understand theoretically why the experimental curve A should have a point of inflexion in the neighbourhood of $x = 3$. The interchange of energy between the moving electron and the radiation will depend on the speed of the electron normal to the atoms of the target, and there seems no justification for assuming that there will be a proportionately large number of electrons giving rise to radiation in the neighbourhood of the point in question.

If we now consider curve B, fig. 2, for which $h = 0{\cdot}3$, $E_m = 7{\cdot}1$, $A = 12{\cdot}6$, $V = 53{\cdot}5$ kv., and $i = 0{\cdot}5$ milliamp., we find $A/E_m = 1{\cdot}776$, and by means of the relation (4) we find $b = 0{\cdot}695$, $c = 9{\cdot}38$, whence, by (2), we obtain $a = 9{\cdot}45$.

We thus find

$$y = 9{\cdot}45(e^{-0{\cdot}695x} - e^{-9{\cdot}38x}) \quad . \quad . \quad . \quad . \quad (6)$$

as the required relation.

In Table II. the results calculated from (6) are compared with the experimental results.

Table II.

x.	y calculated from (6).	y observed.
0·1	5·12	5·3
0·2	6·77	6·8
0·3	7·10	7·10
0·5	6·605	6·5
1·0	4·71	4·85
2·0	2·46	3·1
3·0	1·17	1·35
4·0	0·585	0·25

Curve B′, fig. 2, shows the results obtained from the relation (6). Here again the agreement between the observed and calculated curves is quite good.

We can thus state that the curves given by the general relation

$$y = a(e^{-bx} - e^{-cx}),$$

where the constants are determined in the above manner, represent to a very close approximation the curves observed experimentally.

Application to Varying Potentials.

It will now be shown how this empirical relation can be employed in the calculation of the energy distribution curve for a varying potential of definite period, such as is supplied by most types of high tension machines. For a practical illustration the case of a sinusoidal potential which has been rectified, so that both halves of the wave are operative, will be considered. The case of a more complicated wave form can be treated in a similar manner.

Consider, then, a sinusoidal potential for which

$$V_{max.} = 72{\cdot}1 \text{ kv.} \quad \text{and} \quad i = 0{\cdot}95 \text{ milliamp.},$$

the current being constant. If we regard the half period as a unit of time, then provided this is sufficiently small compared with the time taken for measuring the intensity of the radiation emitted, we can regard the actual voltage as being equivalent to a number of components acting for definite fractions of the time unit, during each of which the voltage may be regarded as constant.

Fig. 3.

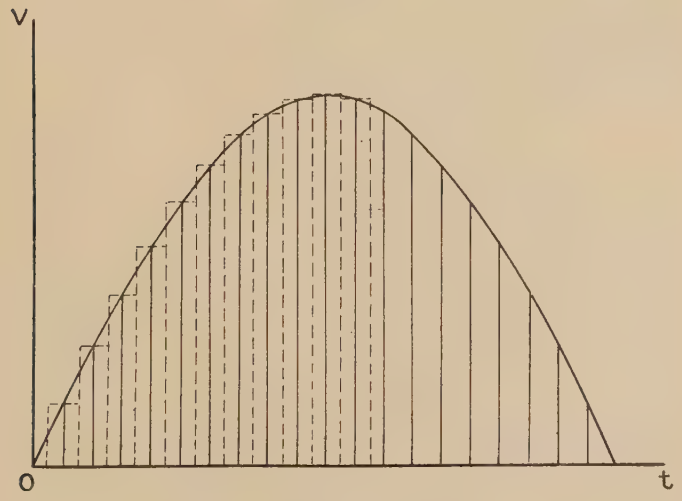


Fig. 3 shows the subdivision of the half period into twenty intervals. The corresponding ordinates at the ends of the intervals, in terms of the maximum ordinate, 72·1, are : 11·27, 22·3, 32·7, 42·4, 51, 58·4, 64·3, 68·6, 71·3, 72·1, etc. respectively. If we now further subdivide the curve as

shown by the dotted lines, we can state that the effect of the actual voltage will be equal to the sum of the following effects :—

(i.) One-twentieth of the effect of the constant potential 72·1 kv. and 0·95 milliamp.

(ii.) One-tenth of the effects of each of the following constant potentials and currents :—71·3 kv., 0·95 ma. ; 68·6 kv., 0·95 ma., etc.

It is not necessary to consider seriously the effects of the voltages 11·27 and 22·3 kv., as these do not affect the position or intensity of the maximum. The calculation of each of the above effects can be very rapidly made. As illustration, the case of the first component will be worked out, and the results for the remaining components quoted. The same scale of ordinates will be preserved as in fig. 2, so that to obtain the distribution curve for any component for 0·95 ma. it is first necessary to find the curve for 0·5 ma. and then to multiply the ordinates by 1·9.

From the curves of fig. 2 we have

$$E_{0\cdot} = kV^2,$$

$$A_{0\cdot5} = k_1V^3,$$

where $E_{0\cdot5}$, $A_{0\cdot5}$, mean the maximum energy and area corresponding to a current 0·5 ma.

From curve A, fig. 2, we find

$$k = \frac{E_{0\cdot5}}{V^2} = \frac{12\ 54}{(71)^2} = 0\cdot00249,$$

$$k_1 = \frac{A_{0\cdot5}}{V^3} = \frac{28\ 71}{(71)^3} = 0\cdot0000805,$$

while from curve B we find

$$k = 0\cdot00248,\ k_1 = 0\cdot0000823.$$

We can thus take

$$k = 0\cdot00249,\ k_1 = 0\cdot0000815.$$

Now for 72·1 kv., 0·5 ma. acting continuously, the maximum energy $E_{0\cdot5}$ is given by

$$E_{0\cdot5} = (72\cdot1)^3 \times 0\cdot00249$$

$$= 12\cdot95,$$

and for a current 0·95 ma. we obtain for the maximum energy

$$E_m = 24\cdot6.$$

Also

$$A_{0\cdot5} = (72\cdot1)^3 \times 0\cdot0000815$$
$$= 30\cdot5.$$

Hence

$$A/E_m = \frac{A_{0\cdot5}}{E_{0\cdot5}} = 2\cdot35.$$

Since

$$\frac{e^{0\cdot3b}}{b} = \frac{e^{0\cdot3c}}{c} = 2\cdot35,$$

we find $b = 0\cdot5$, $c = 10\cdot8$, and hence $a = 29\cdot9$.

The formula for y now becomes

$$y = 29\cdot9(e^{-0\cdot5x} - e^{-10\cdot8x}),$$

and Table III. gives the value of y corresponding to values of x.

TABLE III.

x	0·5	1·0	2·0	3·0	4·0	5·0	6·0
y	23·1	18·1	11·0	6·67	4·05	2·44	1·49

Now,

$$\lambda_0 = \frac{12\cdot348}{72\cdot1} = 0\cdot171 \text{ Å.U.},$$

and hence

$$\lambda_m = 1\cdot3\lambda_0 = 0\cdot222 \text{ Å.U.}$$

Also $\lambda = \lambda_0(1+x)$, and hence for the above values of x we find the following respective values of λ:—0·256, 0·343, 0·513, 0·684, 0·855, 1·026, 1·197 Å.U.

Since the supposed effect of this potential is only one-twentieth of the effect as calculated, it follows that on an energy wave-length graph we must plot the values given in the following Table IV.

TABLE IV.

λ	0·171	0·222	0·256	0·343	0·513	0·684	0·855	1·026
E	0	1·23	1·15	0·91	0·55	0·33	0·20	0·12

In exactly the same way we can calculate the effects of the other component potentials acting for their respective

times. The results of these calculations are summarized in Table V.

TABLE V.

Voltage in kilovolts.		Energy wave-length coordinates.							
71·3...	λ	0·173	0·2255	0·26	0·346	0·519	0·692	0·865	1·038
	E	0	2·4	2·27	1·78	1·1	0·66	0·4	0·24
68·6...	λ	0·18	0·234	0·27	0·36	0·54	0·72	0·90	1·08
	E	0	2·24	2·12	1·64	0·975	0·58	0·345	0·205
64·3...	λ	0·192	0·25	0·288	0·384	0·576	0·768	0·96	1·152
	E	0	1·96	1·805	1·375	0·792	0·453	0·26	0·15
58·4...	λ	0·212	0·276	0·318	0·424	0·636	0·828	1·06	1·272
	E	0	1·61	1·51	1·12	0·6	0·32	0·17	0·09
51·0...	λ	0·242	0·315	0·362	0·484	0·726	0·968	1·21	1·452
	E	0	1·32	1·212	0·822	0·362	0·16	0·07	0·03
42·4...	λ	0·292	0·38	0·438	0·584	0·876	1·168	1·46	1·752
	E	0	0·85	0·69	0·45	0·17	0·07	0·03	0·01

For the potential 32·7 kv. it is sufficient to plot the points $\lambda = 0{\cdot}378$, $E = 0$, and $\lambda = 0{\cdot}51$, $E = 0{\cdot}51$, while for the potential 22·3 kv. it is sufficient to plot the points $\lambda = 0{\cdot}55$ $E = 0$, $\lambda = 0{\cdot}8$, $E = 0{\cdot}236$.

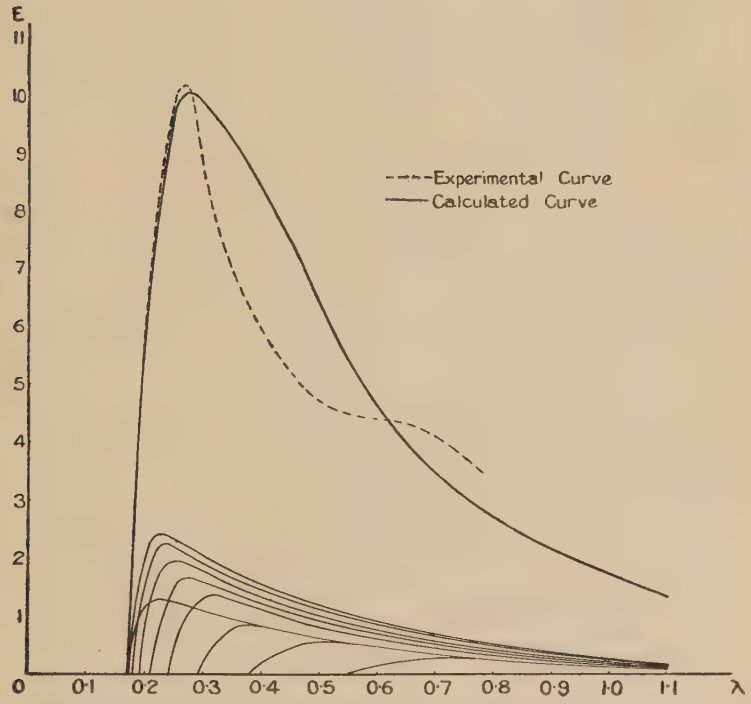
The results given in Tables IV. and V. and the preceding results have been plotted in fig. 4, on which is also drawn the sum of the ordinates of the component curves. This integral curve has the following characteristics :—

$$\lambda_0 = 0{\cdot}171 \text{ Å.U.}, \lambda_m = 0{\cdot}27 \text{ Å.U.}, E_m\, 10{\cdot}1 \text{ units.}$$

The direct observation of the energy distribution curve for a sinusoidal voltage of frequency 50 per second, for which $V_{max.} = 72{\cdot}1$ kv., $i = 0{\cdot}95$ ma., has been made by Dauvillier (p. 75) for a Coolidge tube furnished with a radiator. He finds $\lambda_0 = 0{\cdot}171$ and $\lambda_m = 0{\cdot}26$ Å.U. For the same tube Dauvillier gives a curve for a constant potential 65·6 kv. and current 0·6 ma., and the ratio of the maximum energies of the two curves is approximately 0·795.

Now according to the above arbitrary choice of units for the measurement of energy, a standard Coolidge tube under a constant potential 65·6 kv. and current 0·6 ma. should have a maximum energy 12·9. Hence, the ratio E_m for the sinusoidal potential to E_m for the constant potential is $10·1/12·9 = 0·784$, and the agreement with the observed

Fig. 4.



ratio is well within the limit of experimental error. We can thus state that the empiric method gives the maximum energy in magnitude and position to an extremely good approximation. In the above calculations the potential wave has been divided into twenty intervals. The results obtained by a division into ten intervals only are in very good agreement with the above results, and hence for most practical purposes a subdivision into ten intervals is sufficient.

The curve obtained by Dauvillier (curve B, p. 75) is shown in fig. 4 by the broken line. Comparing with the integral curve obtained above we find that the curves diverge

to the right of the maximum, the empiric curve lying above the observed curve. Hence, the empiric curve has a larger area than the observed curve. This difference may possibly be due to the use of a tube with a radiator, for if the constant potential curve for 65·6 kv., 0·6 ma. is drawn in the form of the x, y graph to the arbitrary scale used throughout, it is found that while the maximum energy satisfies the relation $E_m = kV^2$, the area of the curve falls short of the relation $A = k_1V^3$ by about 25 per cent. It thus seems likely that a standard tube under the sinusoidal potential and the current that has been examined should give greater energies to the right of the maximum than the radiator tube, and hence the agreement with the calculated curve will indeed be much better.

Extensions of the Method.

The problem of determining the energy distribution curve when the form of the potential wave is less regular is solved in the same way as the above case. It is, of course, necessary to know the mean current through the tube and the maximum potential, and to have an oscillograph record of the potential wave. The experimental difficulties connected with this latter determination are very small, and the time taken to obtain a record will not disturb the routine of a large X-ray therapy department. The method used by Crowther*, for example, is a very convenient one.

The whole of this discussion applies only to the continuous spectrum from a standard Coolidge tube. At the present stage it is not possible to consider the effect of the characteristic radiations for the reason that no experimental curves have been determined for constant potentials and corrected, as Dauvillier has done, to represent the true radiation from the target alone. Further, the radiations from a tube with a radiator, or a water-cooled tube, appear to obey laws slightly different from the radiations from a standard tube, and as these laws have not been investigated, we can at present only approximate to the radiations that they emit. For a gas tube the problem seems much more difficult, but

* Crowther. *loc. cit.*, and also Camb. Phil. Soc. Proc. xxii. p. 68 (1924). Crowther shows that for a maximum potential of 73 kv. for a rectified transformer discharge, the current reaches saturation for a very small potential but increases slightly, probably due to the dragging out of additional electrons from the filament by the strong electrostatic field. This effect will probably be increased for higher voltages, and it thus seems advisable to obtain simultaneous records of the potential and current waves, as Crowther has done.

with systematic results it should not be insurmountable. What is most urgently required is a complete study of the radiations from all types of tubes under constant potentials from 30 kv. to 200 kv., say. The laws governing the continuous and the characteristic radiations could then be studied, and the determination of the energy distribution could be made a matter of precision. In addition it would be possible to state precisely, from a study of the oscillograph records, what potential and what current must be used to produce a maximum energy at a given wave-length.

The chief difficulty in any such systematic study lies in the generation of a constant potential. For moderate potentials a battery has been employed *, but for the high potentials required in therapy treatment a battery is out of the question. The only method of such production is thus reduced to a form of high tension generating machine. Several devices have been suggested for generating an approximately constant potential. Ulrey † employed a step-up transformer using two kenotrons to rectify the current, and reduced the fluctuations by a specially-designed condenser, as suggested by Hull ‡. No oscillograph records are shown, and the probability is that for very high tensions the fluctuations would be large. Dauvillier § obtained a high potential by the rapid charge of a condenser, but does not consider that it would be possible to obtain 150 to 200 kv. in this way. Kirkpatrick ‖ used a synchronous shutter between the tube and the spectrometer to admit only the radiations corresponding to the peak voltage. This form of potential can hardly be called constant. More recently, Moore¶ has described a machine which is capable of producing high potentials which are very nearly constant, the oscillograph record showing small fluctuations about a constant mean. It is probably from machines of this type that we may expect to obtain the ideal form of potential. There is a growing tendency in X-ray practice to employ constant potential machines, and if this tendency becomes the rule a very large gap in the standardization of treatment will have been bridged.

* Duane and Hunt, Phys. Rev. vi. p. 166 (1915).
† Ulrey, Phys. Rev. xi. p. 401 (1918).
‡ Hull, Phys. Rev. vii. p. 156 (1916).
§ Dauvillier, *Comptes Rendus*, clxii. p. 405 (1916).
‖ Kirkpatrick, *loc. cit.*
¶ Moore, Journ. Ront. Soc. (Brit. Journ. Radiology) xx. p. 73 (1924).

Finally, it is of interest to note that Moppett * has found evidence of a differential action of rays of varying wave-length on animal tissue. Using a Bragg spectrometer, adapted so that approximately equal energy was employed for each wave-length, he found that complete atrophy was produced in the chorio-allantoic membrane of eight-day chick embryos at the definite wave-lengths 0·11, 0·53, and 0·79 A.U. The effect was sharply restricted to these wave-lengths, the greatest effect occurring for the shortest wave-length. He concludes that the clinical uses of X-rays all correspond to stimulation by different wave-lengths. These results seem to indicate the necessity for a revision of the customary methods of dosage, as suggested earlier in the paper.

Summary.

1. From the corrected experimental curves given by Dauvillier for a standard Coolidge tube under different constant potentials and currents, an empirical expression of the form

$$y = a(e^{-bx} - e^{-cx})$$

has been found to represent the energy distribution curve with considerable accuracy.

2. By subdividing the form of a sinusoidal potential wave into a number of intervals during which an appropriate constant potential is supposed to act, the application of the empirical expression produces an integral distribution curve, which agrees very well with an experimental curve given by Dauvillier for approximately equal conditions.

3. It is suggested that the energy distribution curve can, in the same way, be predicted when the forms of the potential and current waves are known.

4. The importance of the knowledge of the energy distribution curve for any type of machine in its application to clinical practice is stressed, and the method of standardizing treatment in terms of the characteristics of the energy distribution curve is suggested as being more precise than the former method of subjecting the patient to a certain number of erythema doses.

The remarks in this paper must necessarily be taken as preliminary on account of the relatively small amount of knowledge of the standard cases. As has been pointed out,

* Moppett, The Medical Journal of Australia, i. no. 15, p. 364 (1925).

a complete discussion can only follow from thoroughly corroborated investigations of the energy distribution curves for different types of tubes under constant potentials up to 200 kilovolts. It is hoped shortly to obtain equipment in this University that will permit such an investigation.

It is a pleasure to thank Prof. T. H. Laby, Sc.D., who suggested the investigation, and Prof. J. H. Michell, F.R.S., for helpful suggestions during the course of this research.

[I am indebted to Dr. Dauvillier for drawing my attention, after he had read the above in manuscript, to a paper by Behnken on the same subject—a paper which was not accessible to Mr. Belz. References to Behnken's papers have been added.—T. H. L.]

The University,
Melbourne.
July 13, 1925.

V. *A supposed Relativity Method of Determining the Size of a Gravitating Particle.* *By* Prof. H. T. H. Piaggio, *M.A., D.Sc., and* J. Critchlow, *B.Sc., University College, Nottingham* *.

Introduction.

A PARTICULAR solution of Einstein's gravitational equations for an isolated particle is the well-known form, first obtained by Schwarzschild,

$$ds^2 = -\gamma^{-1}\,dr^2 - r^2\,d\theta^2 - r^2\sin^2\theta\,d\phi^2 + \gamma\,dt^2, \quad . \quad (1)$$

where $\gamma = 1 - 2m/r$.

m is a constant subsequently identified with the mass of the particle.

Now when r has the value $2m$, the coefficient of dr^2 in (1) is infinite. This result has generally been interpreted as showing that an impassable barrier exists of radius $2m$, and thus that a particle must have a definite size determined by its mass.

The object of this paper is to give reasons for rejecting this interpretation, and for considering the singularity as a purely mathematical property of a certain transformation of coordinates, without any physical significance. It will be shown that alternative solutions exist, which satisfy all the physical tests applicable and yet do not exhibit this singularity. One of these solutions was actually given by

* Communicated by the Authors.

Schwarzschild himself. It will be pointed out that although one solution can always be transformed into another, this transformation is not valid for all values of the variable.

In the usual method of obtaining (1) this limitation is overlooked. The apparent singularity arises when we attempt to give the variable a value for which the transformation is illegitimate.

Alternative Solutions of the Gravitational Equations for an Isolated Particle.

The simplest method of obtaining alternative solutions is to transform (1) by the relation

$$r=f(\mathrm{R}).$$

We must now consider what forms for the function f are physically possible. It will be remembered that in the deduction of (1), r, θ, ϕ, t are at the outset merely four variables whose exact significance is unknown. When we endeavour to identify them with the ordinary polar coordinates and the time, we take our solution and see if it satisfies the following requirements :—

(i.) it must possess spherical symmetry in space ;

(ii.) it must possess symmetry as regards past and future time ;

(iii.) for very large values of r it must tend to the form $ds^2=-dr^2-r^2\,d\theta^2-r^2\sin^2\theta\,d\phi^2+dt^2$;

(iv.) it must, when applied to the sun, agree with the Newtonian theory and ordinary astronomical observations to the first order ;

(v.) it must give, as second order effects, the advance of the perihelion of Mercury, the deflexion of light passing near the sun, and the spectral shift observed for the sun and for the companion of Sirius.

Now these requirements are satisfied by Schwarzschild's solution, but they are also satisfied by other solutions. A well-known example is Hill and Jeffery's isotropic solution

$$ds^2=-(1+m/2\mathrm{R})^4(d\mathrm{R}^2+\mathrm{R}^2\,d\theta^2+\mathrm{R}^2\sin^2\theta\,d\phi^2)+\left\{\frac{1-m/2\mathrm{R}}{1+m/2\mathrm{R}}\right\}^2 dt^2, \quad . \quad . \quad (2)$$

which can be obtained from (1) by the transformation

$$r=(1+m/2\mathrm{R})^2\mathrm{R}.$$

This is more complex mathematically than (1), but it satisfies all the requirements stated above. As Eddington * says, "this system of coordinates is naturally arrived at when we partition space by rigid scales or by light-triangulations in a small region, *e. g.* in terrestrial measurements." From a physical point of view the R of (2) has therefore at least as good a claim to be identified with the actual radius vector from the sun as the r of (1). Of course in either case the identification cannot be exact, for when we speak of the actual radius vector we are tacitly assuming a Euclidean universe, whereas Einstein's equations imply that it is non-Euclidean.

The isotropic solution is the best known of the alternative solutions, but others are easily obtained by the transformation $r=f(\mathrm{R})$, where the only limitation on the form of the function is that the limit of the ratio r/R should be unity as r approaches infinity.

By putting $r=(\mathrm{R}^2+4m^2)^{1/2}$, (1) becomes

$$ds^2=-\{1+2m(\mathrm{R}^2+4m^2)^{-1/2}\}\,d\mathrm{R}^2 - (\mathrm{R}^2+4m^2)(d\theta^2+\sin^2\theta\,d\phi^2)+\{1-2m(\mathrm{R}^2+4m^2)^{-1/2}\}dt^2. \quad . \quad . \quad . \quad . \quad (3)$$

Similarly by putting $r=(\mathrm{R}^3+8m^3)^{1/3}$, (1) becomes

$$ds^2=-\frac{(\mathrm{R}^3+8m^3)^{-4/3}\mathrm{R}^4\,d\mathrm{R}^2}{1-2m(\mathrm{R}^3+8m^3)^{-1/3}}-(\mathrm{R}^3+8m^3)^{2/3}(d\theta^2+\sin^2\theta\,d\phi^2) +\{1-2m(\mathrm{R}^3+8m^3)^{-1/3}\}dt^2. \quad . \quad (4)$$

More generally, we could put

$$r=(\mathrm{R}^n+2^n m^n)^{1/n}.$$

It is sometimes overlooked that (1) is not the solution that Schwarzschild originally obtained. On referring to his paper †, we find that he started with a somewhat complicated solution in x_1, x_2, x_3, x_4. By putting

$$x_1=r^3/3, \quad x_2=-\cos\theta, \quad x_3=\phi, \quad x_4=t,$$

he obtained a second form

$$ds^2=-\frac{(r^3+\rho)^{-4/3}r^4\,dr^2}{1-\alpha(r^3+\rho)^{-1/3}}-(r^3+\rho)^{2/3}(d\theta^2+\sin^2\theta\,d\phi^2) +\{1-\alpha(r^3+\rho)^{-1/3}\}dt^2 \quad . \quad . \quad (5)$$

containing the two constants α and ρ.

* 'Mathematical Theory of Relativity,' p. 93.

† *Berlin. Sitzungsberichte*, 1916, p. 189; most of it is reproduced in Rice's 'Relativity,' pp. 271-276.

Finally, by writing $R=(r^3+\rho)^{1/3}$, he obtained a form equivalent to (1).

It will be noticed that if we put $\rho=\alpha^3=(2m)^3$, (5) reduces to (4).

Comparison of these Solutions.

As we noted at the outset, the coefficient of dr^2 in (1) becomes infinite when $r=2m$. In (2) the coefficient of dR^2 becomes infinite for $R=0$, but not for any positive value of R. In (3) and (4) the coefficient of dR^2 is always finite for positive values of R. (5) cannot be discussed until we know the sign of $\rho-\alpha^3$.

Thus the singularity that appears in (1) does not appear in the other forms that are equally in accord with the only physical evidence available, and it is repugnant to the spirit of relativity to attach a physical interpretation to a property of a special form of coordinates.

Similar considerations apply to the coefficient of dt^2. In (1) this coefficient becomes zero when $r=2m$, and tempts us to speak of a standstill of time at this region ; but again we reject this interpretation upon noticing that the coefficient of dt^2, which may vanish in (1) or (2), cannot do so in (3) or (4) for any positive value of R.

Limitations to the Validity of Transformations.

We shall now consider how it is that Schwarzschild's third form (1) exhibits a singularity which, when $\rho-\alpha^3$ is positive or zero, is not possessed by his second form (5).

The transformation he used, namely

$$R=(r^3+\rho)^{1/3},$$

imposes a distinct limitation upon R. Since r is, for a physical interpretation, restricted to real positive values from 0 to ∞, R has a minimum value $\rho^{1/3}$. If we take $\rho=\alpha^3$, a very natural assumption, designed to give (5) a singularity at $r=0$, where it might be expected, we unconsciously introduce a singularity into (1) for the corresponding value α $(=2m)$ of R.

It is more usual now to obtain Schwarzschild's third form directly *. Starting with the form

$$ds^2=-U(r)\,dr^2-V(r)(r^2\,d\theta^2+r^2\sin^2\theta\,d\phi^2)+W(r)\,dt^2,$$

a simplification is introduced by the transformation

$$r_1^2=r^2V(r). \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

* *Cf.* Eddington, p. 83.

This transformation may only be valid for a restricted range of values of r. For example, if $V(r)=1+4m^2/r^2$,

$$r_1^2=r^2+4m^2.$$

In this case r_1 cannot be less than $2m$. It is therefore natural that a singularity should arise when $r_1=2m$, whereas in the more general form such a singularity might have been present only at the obvious point $r=0$.

Summary.

A singularity in Schwarzschild's solution of Einstein's equations which has been widely interpreted as indicating a definite size for a gravitating particle, is shown to be merely a mathematical property of a transformation of coordinates, without any physical significance.

Nottingham,
October 10th, 1925.

VI. *On the Concentration of Stress in the Neighbourhood of a Small Spherical Flaw; and on the Propagation of Fatigue Fractures in "Statistically Isotropic" Materials.* *By* R. V. Southwell, *M.A., F.R.S., and* H. J. Gough, *M.B.E., B.Sc., of the National Physical Laboratory* *.

1. THE mathematical theory of elasticity, as at present developed, predicates two essential qualities in the ideal substances with which it is concerned: they must be *elastic*, so that the deformation produced by any system of applied forces will disappear when that system is removed; and they must be *continuous*, so as to be capable of indefinite subdivision without losing any property which they exhibit in bulk.

It is probable that those characteristics of real substances which are described by the terms "plasticity" and "hysteresis" will in time, by suitable extensions of the theory, be brought within its scope †; but the assumption of continuity appears to be fundamental, and results which have this basis should be applied with considerable reserve to actual cases

* Communicated by the Authors.

† A beginning has been made by Volterra and others. *Cf.* A. E. H. Love, 'Mathematical Theory of Elasticity', § 82 and footnote; L. Prandtl, *Zeitsch. für angewandte Math. u. Mech.*, vol. iii, pp. 401–406 (1923); H. Hencky, *ibid.*, vol. iv, pp. 323–334 (1924); and a paper in 'Engineering', Aug. 23, 1912.

of stress-concentration, because the structure of the material must be expected to play an important part*. Thus we cannot look for much direct assistance from theory when attacking such problems as the mechanism of fracture in engineering materials or the factors which limit their ultimate strength. Fracture is a consequence of high stresses,—presumably (since it occurs under average stresses which are far below the calculated "cohesion") of intense local concentration of stress ; and we know that most engineering materials are aggregates of metallic crystals which individually are very far from being isotropic, and which are arranged at random, without any tendency towards a definite orientation. We cannot say in advance how the planes of greatest weakness will lie in a given region of concentrated stress : their direction may be such as will relieve the stress-concentration, but it is equally likely to have no such effect. We are in a field of problems where exact calculations can have no place, and occurrences are governed by probabilities.

In this field, on the other hand, the mathematical theory may still have some value as a statistical method. The crystalline aggregate is in general statistically homogeneous, and unless the individual crystals have been violently distorted by special treatment, such as "cold work", it will also be statistically isotropic. Alternating or fluctuating stresses, which produce distortion of the material as a whole, are not likely to have seriously affected this statistical homogeneity and isotropy of the aggregate, even though they are sufficiently intense to have caused some plastic slipping †. Thus the theory, although it can give no trustworthy indication of the actual stresses which have brought about failure in any particular instance, may be used with some confidence to determine *the relative values of their probable intensities at different points in the material* ; and in this way it may serve to elucidate the sequence of events in a given fracture, or even to suggest, as a matter of probabilities, its primary cause.

2. An attempt to apply the mathematical theory in this way was made by one of us in 1921, in a paper written for the Materials Sub-Committee of the Aeronautical Research

* *Cf.* A. A. Griffith, Phil. Trans. Roy. Soc. A, vol. 221. p. 193 (1920).

† For the argument of this paper, it is only necessary to assume that the crystalline structure is sensibly uniform in kind over regions which are large in comparison with individual crystals. This assumption may not be justified in the neighbourhood of a skin formed by the process of "case-hardening", or in regions where localized plastic strain has occurred under an intense concentration of stress.

Committee on the subject of "spiral fractures" in the propeller shafts of aero-engines. Prof. C. F. Jenkin, in his Presidential Address to Section G at the 1920 meeting of the British Association, had directed attention to a fracture of this nature (illustrated in fig. 1 *) as a phenomenon which had not so far received a satisfactory explanation, although possessing great interest and practical importance from the point of view of the designer. "It is, of course, a fatigue fracture—*i. e.*, it spread gradually. The questions to be answered are, Did it fail under tension, bending or torsion? and, Why was a spiral direction followed by the failure as it spread?" †

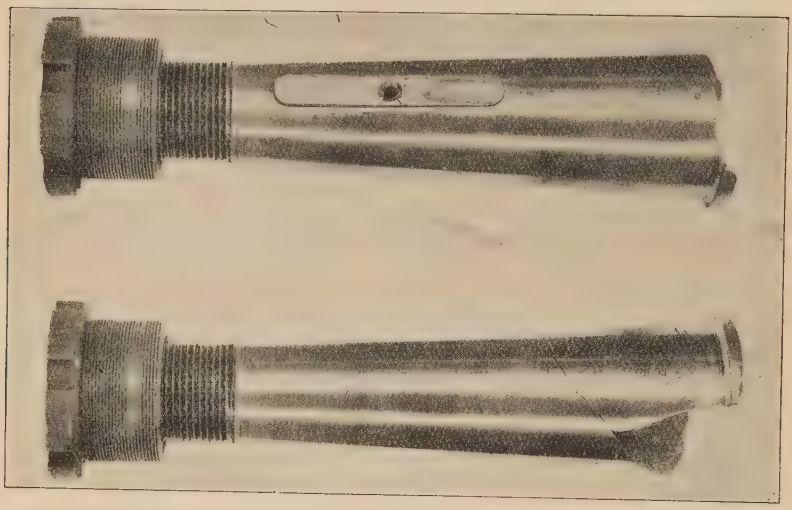
It seemed fairly clear (since there was no reason to believe that the helicoidal surface of the fracture had been a surface of special weakness in the shaft when new) that the crack had followed a path which was determined primarily by the distribution of stress in the material; and a consideration of probabilities, based on a theoretical solution for the stress-distribution round a small spherical flaw in isotropic elastic material, indicated that a fatigue fracture, *in material which is statistically isotropic*, has a strong tendency to spread along a surface which is tangential at every point to the plane of the greatest principal tensile stress. On the basis of this result, it appeared that the answers to Prof. Jenkin's questions could be stated as follows:—The action which induced his "spiral fracture" was in the main torsional. Tension, bending, or compression may have contributed in a minor degree, and an idea of the relative importance of these actions in any particular instance could be obtained from an examination of the direction followed by the fracture. Failure began at some point where there was an intense local concentration of stress (probably caused by a flaw in the material, or by a surface scratch), and a "spiral" direction was followed by the failure (*i. e.*, the surface of separation is, in its general features, helicoidal) because the tensile stresses induced by torsion attain their maximum values on a surface of this type.

To prevent misunderstanding, it was emphasized that the existence of a localized crack in an elastic solid body must modify to some extent, and may alter very considerably, the stress-distribution which a given system of applied forces will entail; thus it is not certain that we shall be able to

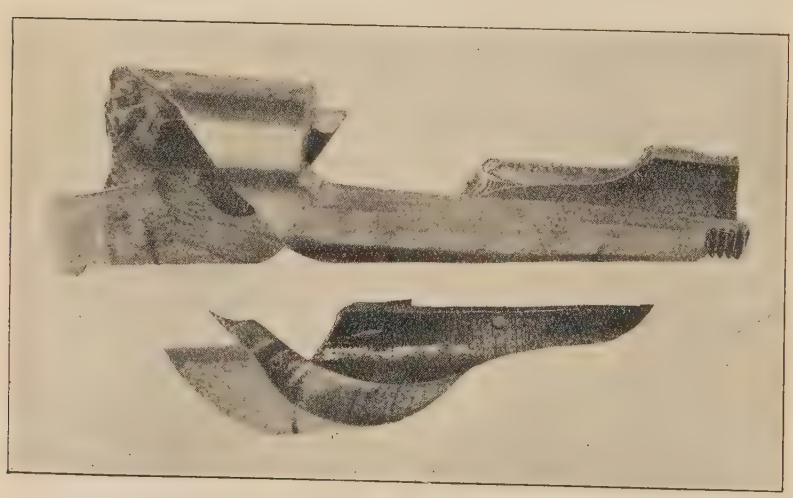
* We are indebted to Prof. Jenkin for the loan of the photographs reproduced in this figure. Other photographs of typical fractures are given in the plate facing p. 16 of his 'Report on Materials of Construction used in Aircraft and Aircraft Engines' (1920).

† British Association Report, 1920, p. 131.

Fig. 1.



Spiral Fracture in Crankshaft, commencing at the bottom corner of the Keyway.



The same shaft, cut open.

foretell the path of a fatigue fracture, provided only that we can calculate the theoretical stress-system which obtains before any crack has formed. But within its limitations it appeared that the theory should prove useful in the diagnosis of fatigue fractures ; and conversely, that an examination of a large number of fatigue fractures might be expected to reveal more clearly what these limitations are.

3. These conclusions, and the arguments by which they were reached (stated more fully in §§ 4 to 8 below), were generally accepted. The paper mentioned has been the subject of considerable discussion by the Elasticity and Fatigue Panel of the Aeronautical Research Committee, aimed in the main at determining what, if any, is the bearing of its results upon the more difficult question of the *origin* of fatigue fractures ; and arising out of this discussion certain experiments have been conducted in the Engineering Department of the National Physical Laboratory. The present paper has been written at the request of the Panel, to summarize the position now attained. We are conscious that our ideas have been largely influenced by those of other members, to whom (and especially to Dr. A. A. Griffith) we desire to express our indebtedness ; but it should be emphasized that the Panel is not in any way responsible for the views herein expressed.

Our thanks are also due to Miss C. G. C. Phillips, who prepared the line diagrams which illustrate this paper.

Part I.—The Propagation of Fatigue Fractures.

Stress-Concentration produced by a Small Spherical Flaw in Material subjected to Uniform Tension.

4. We require first of all to determine the stress-system which obtains in the neighbourhood of a small spherical flaw when the stress at points far away from the flaw is a uniform tension T in one direction only. This is a problem of symmetrical strain in a solid of revolution *, and the stress-equations of equilibrium, expressed in terms of cylindrical coordinates r, θ, z, are

$$\left.\begin{aligned} \frac{\partial \widehat{rr}}{\partial r} + \frac{\partial \widehat{rz}}{\partial z} + \frac{\widehat{rr} - \widehat{\theta\theta}}{r} &= 0, \\ \frac{\partial \widehat{rz}}{\partial r} + \frac{\partial \widehat{zz}}{\partial z} + \frac{\widehat{rz}}{r} &= 0. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

* *Cf.* Love, *op. cit.*, § 188.

It can be verified by substitution that these stress-equations will be satisfied if we assume *

$$\left.\begin{aligned} \widehat{rr} &= \frac{\partial}{\partial z}\left\{\sigma\nabla^2\chi - \frac{\partial^2\chi}{\partial r^2}\right\}, \\ \widehat{\theta\theta} &= \frac{\partial}{\partial z}\left\{\sigma\nabla^2\chi - \frac{1}{r}\frac{\partial\chi}{\partial r}\right\}, \\ \widehat{zz} &= \frac{\partial}{\partial z}\left\{(2-\sigma)\nabla^2\chi - \frac{\partial^2\chi}{\partial z^2}\right\}, \\ \widehat{rz} &= \frac{\partial}{\partial r}\left\{(1-\sigma)\nabla^2\chi - \frac{\partial^2\chi}{\partial z^2}\right\}, \end{aligned}\right\} \quad . \quad . \quad . \quad (2)$$

where σ is Poisson's ratio, ∇^2 denotes the operator

$$\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2},$$

and χ is a function of r and z which satifies the equation

$$\nabla^4\chi = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Further, it can be shown that the strains deduced from the expressions (2) are compatible. The boundary conditions require that at a great distance from the centre of the spherical flaw

$$\widehat{rr} = \widehat{\theta\theta} = \widehat{rz} = 0, \quad \widehat{zz} = \mathrm{T}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and that the surface of the flaw shall be free from stress.

5. A solution of (2) and (3) which satisfies these boundary conditions is most easily obtained by transformation into spherical coordinates, with origin at the centre of the flaw †. We find as the required expression for the stress-function χ

$$\chi = \mathrm{T}\left[\frac{(1-2\sigma)z^3 + 3\sigma r^2 z}{6(1+\sigma)} - \frac{a^3}{14-10\sigma}\left\{(1-5\sigma)\sinh^{-1}\left(\frac{z}{r}\right) + 5\frac{z}{\mathrm{R}} - \frac{a^2 z}{\mathrm{R}^3}\right\}\right],$$

where a is the radius of the flaw, and

$$\mathrm{R}^2 = r^2 + z^2.$$

This expression can be shown to satisfy (3), and it gives

* *Ibid.*, equations (63) to (65).

† The complete analysis is contained in a paper not yet published, "On some Stress-Systems in Solids of Revolution".

as corresponding expressions for the stress-components (2)

$$\left.\begin{aligned}
\widehat{rr} &= \frac{\mathrm{T}}{14-10\sigma}\cdot\frac{a^3}{\mathrm{R}^3}\Big[9-15\sigma-12\frac{a^2}{\mathrm{R}^2} \\
&\quad -\frac{r^2}{\mathrm{R}^2}\Big(72-15\sigma-105\frac{a^2}{\mathrm{R}^2}\Big)+15\frac{r^4}{\mathrm{R}^4}\Big(5-7\frac{a^2}{\mathrm{R}^2}\Big)\Big], \\
\widehat{\theta\theta} &= \frac{\mathrm{T}}{14-10\sigma}\cdot\frac{a^3}{\mathrm{R}^3}\Big[9-15\sigma-12\frac{a^2}{\mathrm{R}^2} \\
&\quad -15\frac{r^2}{\mathrm{R}^2}\Big(1-2\sigma-\frac{a^2}{\mathrm{R}^2}\Big)\Big], \\
\widehat{zz} &= \mathrm{T}\Big[1-\frac{1}{14-10\sigma}\cdot\frac{a^3}{\mathrm{R}^3}\Big\{38-10\sigma-24\frac{a^2}{\mathrm{R}^2} \\
&\quad -\frac{r^2}{\mathrm{R}^2}\Big(117-15\sigma-120\frac{a^2}{\mathrm{R}^2}\Big)+15\frac{r^4}{\mathrm{R}^4}\Big(5-7\frac{a^2}{\mathrm{R}^2}\Big)\Big\}\Big], \\
\widehat{zr} &= \frac{\mathrm{T}}{14-10\sigma}\cdot\frac{a^3zr}{\mathrm{R}^5}\Big[-3(19-5\sigma)+60\frac{a^2}{\mathrm{R}^2} \\
&\quad +15\frac{r^2}{\mathrm{R}^2}\Big(5-7\frac{a^2}{\mathrm{R}^2}\Big)\Big].
\end{aligned}\right\} \quad . \quad (5)$$

Fig. 2 shows the system of coordinates to which these equations relate. At points in the (r, θ) plane OB, where $z=0$, the foregoing expressions (5) for the stress-components reduce to

$$\left.\begin{aligned}
\widehat{rr} &= \frac{12\mathrm{T}}{14-10\sigma}\cdot\frac{a^3}{\mathrm{R}^3}\Big(1-\frac{a^2}{\mathrm{R}^2}\Big), \\
\widehat{\theta\theta} &= \frac{3\mathrm{T}}{14-10\sigma}\cdot\frac{a^3}{\mathrm{R}^3}\Big(-2+5\sigma+\frac{a^2}{\mathrm{R}^2}\Big), \\
\widehat{zz} &= \mathrm{T}\Big[1+\frac{1}{14-10\sigma}\cdot\frac{a^3}{\mathrm{R}^3}\Big(4-5\sigma+9\frac{a^2}{\mathrm{R}^2}\Big)\Big], \\
\widehat{zr} &= 0,
\end{aligned}\right\} \quad . \quad (6)$$

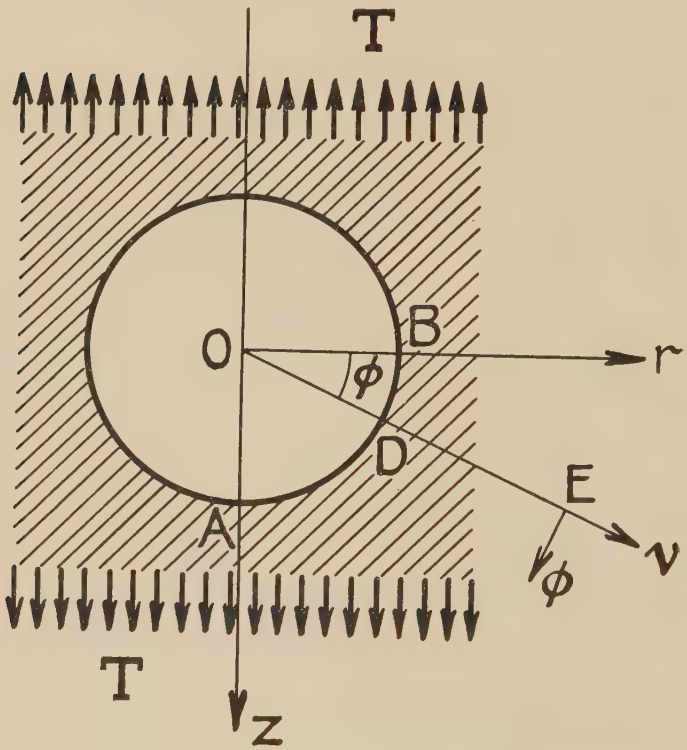
where R is now identical with r.

Making a/R equal to unity in these expressions, we see that at points such as B, where the (θ, z) plane intersects the surface of the flaw, $\widehat{zz}$ has the value $3\,(9-5\sigma)\mathrm{T}/(14-10\sigma)$, which is slightly greater than 2T when $\sigma=0{\cdot}3$ (a representative value for steel). If the flaw had been cylindrical, with its axis perpendicular to the direction of T, the corresponding extreme value of $\widehat{zz}$ would have been 3T *, whence

* *Cf.* A. Morley, 'Strength of Materials' (4th Edition), Appendix, p. 537.

it is clear that the spherical flaw produces a less serious intensification of stress : this result might, of course, have been expected from physical considerations. *In neither case is the intensification dependent on the actual magnitude of the flaw, provided only that this is infinitesimal in comparison with the external dimensions of the elastic solid considered.*

Fig. 2.

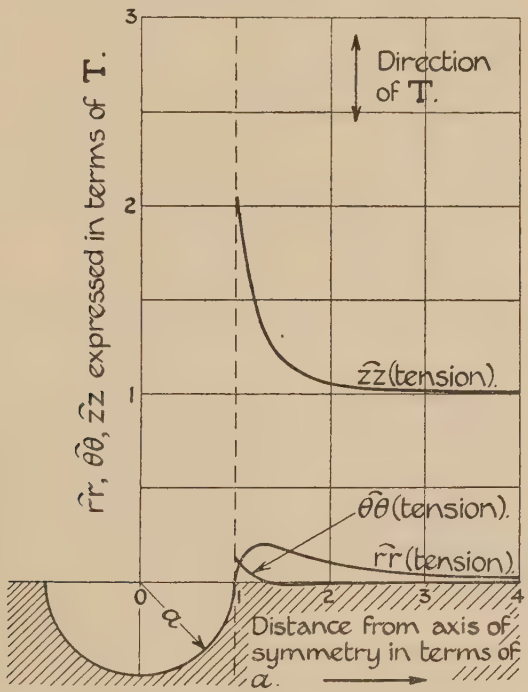


The values of $\widehat{zz}$ at other points in the (r, θ) plane OB are plotted in fig. 3 (σ being given, as before, the value 0·3), together with those of $\widehat{rr}$ and $\widehat{\theta\theta}$ for the same plane. The nature of the variations in $\widehat{rr}$ and $\widehat{zz}$ is generally similar to what is found in the corresponding solution for a cylindrical flaw *, as will be evident from the curves given, for purposes

* *Cf.* A. Morley, *op. cit.*, p. 538.

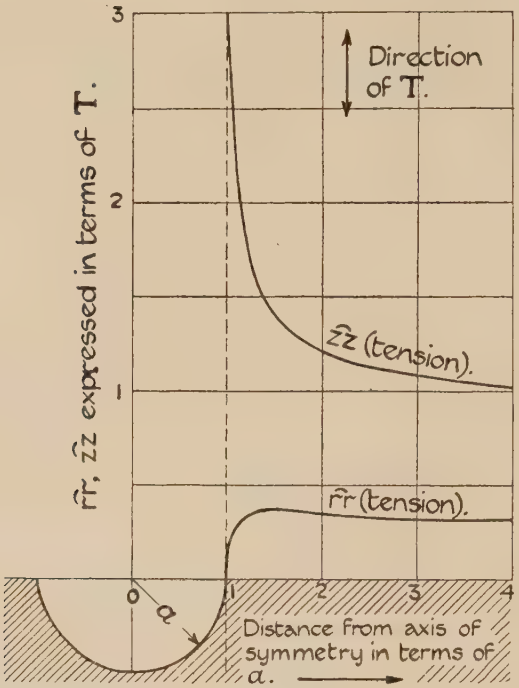
of comparison, in fig. 4. The analytical expressions for the stress-components are, however, much simpler in the latter solution, since they have the property, characteristic of any two-dimensional system in which the tractions on the boundaries are specified, of being independent of the value of σ.

Fig. 3.



From the nature of the curves given in fig. 3, it will be evident that, on any theory of breakdown, the dominant part is played by the increased tension $\widehat{zz}$ at points close to the surface of the flaw. Moreover, we can show that this intensification of stress at the surface is confined to points which are near to the (r, θ) plane,—*i. e.*, to points of which the angular coordinate ϕ (fig. 2) is small. For if we consider a cone of which the trace is ODE (fig. 2), we have, corresponding to the stresses $\widehat{rr}$, $\widehat{\theta\theta}$, and $\widehat{zz}$ for the (r, θ) plane, the stresses $\widehat{\nu\nu}$, $\widehat{\theta\theta}$, and $\widehat{\phi\phi}$ respectively. If the directions

Fig. 4.



of ν, θ and ϕ are as specified in fig. 2, we have the scheme of transformation

	r	θ	z
ν	$\cos\phi$	0	$\sin\phi$
θ	0	1	0
ϕ	$-\sin\phi$	0	$\cos\phi$

,

and from the usual formulæ for transformation of stress-components * we obtain

$$\left.\begin{aligned} \widehat{\nu\nu} &= \widehat{rr}\cos^2\phi + \widehat{zz}\sin^2\phi + \widehat{zr}\sin 2\phi, \\ \widehat{\phi\phi} &= \widehat{rr}\sin^2\phi + \widehat{zz}\cos^2\phi - \widehat{zr}\sin 2\phi, \\ \widehat{\nu\phi} &= \tfrac{1}{2}(\widehat{zz} - \widehat{rr})\sin 2\phi + \widehat{zr}\cos 2\phi. \end{aligned}\right\} \quad . \quad . \quad (7)$$

* A. E. H. Love, *op. cit.*, §49.

Then from (5) and (7) (writing $\cos\phi$ for r/R and $\sin\phi$ for z/R in the former equations) we have, as expressions corresponding to (6),

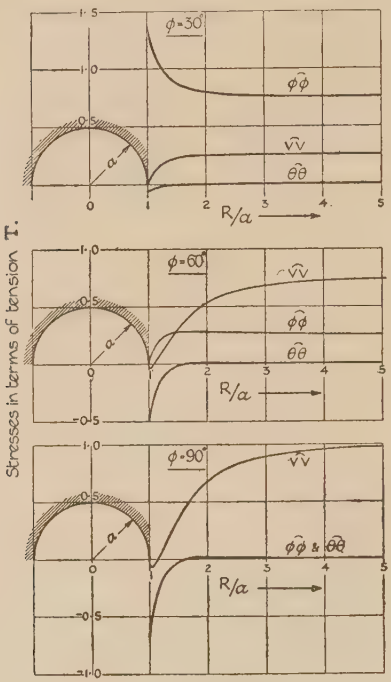
$$\left.\begin{aligned}
\widehat{\nu\nu} &= T\left[\sin^2\phi + \frac{1}{14-10\sigma}\cdot\frac{a^3}{R^3}\left\{-38+10\sigma\right.\right.\\
&\qquad \left.\left.+24\frac{a^2}{R^2}+\left(50-10\sigma-36\frac{a^2}{R^2}\right)\cos^2\phi\right\}\right],\\
\widehat{\theta\theta} &= \frac{T}{14-10\sigma}\cdot\frac{a^3}{R^3}\left[9-15\sigma-12\frac{a^2}{R^2}\right.\\
&\qquad \left.-15\left(1-2\sigma-\frac{a^2}{R^2}\right)\cos^2\phi\right],\\
\widehat{\phi\phi} &= T\left[\cos^2\phi+\frac{1}{14-10\sigma}\cdot\frac{a^3}{R^3}\left\{9-15\sigma-12\frac{a^2}{R^2}\right.\right.\\
&\qquad \left.\left.-\left(5-10\sigma-21\frac{a^2}{R^2}\right)\cos^2\phi\right\}\right],\\
\widehat{\nu\phi} &= \frac{T}{2}\sin 2\phi\left[1\right.\\
&\qquad \left.+\frac{1}{14-10\sigma}\cdot\frac{a^3}{R^3}\left\{10(1+\sigma)-24\frac{a^2}{R^2}\right\}\right].
\end{aligned}\right\} \quad . \quad (8)$$

Curves similar to those of fig. 3 can now be plotted for any value of ϕ, and fig. 5 shows the forms which they assume when $\phi=30°$, $60°$, and $90°$. At the surface of the flaw the stress-components attain values given by

$$\left.\begin{aligned}
[\widehat{\nu\nu}]_{R=a} &= [\widehat{\nu\phi}]_{R=a}=0,\\
[\widehat{\theta\theta}]_{R=a} &= \frac{3T}{14-10\sigma}\left[-(1+5\sigma)+10\sigma\cos^2\phi\right],\\
[\widehat{\phi\phi}]_{R=a} &= \frac{3T}{14-10\sigma}\left[-(1+5\sigma)+10\cos^2\phi\right],
\end{aligned}\right\} \quad . \quad (9)$$

and fig. 6, in which the values reached by $\widehat{\theta\theta}$ and $\widehat{\phi\phi}$ at the surface of the flaw are exhibited by means of a polar diagram, shows clearly the extent to which the intensification of the stresses is a localized effect. It is evident that the maximum stress, strain and stress-difference will occur at points such as B on the (r, θ) plane in fig. 2, so that a fracture may be expected to start at one of these points.

Fig. 5.



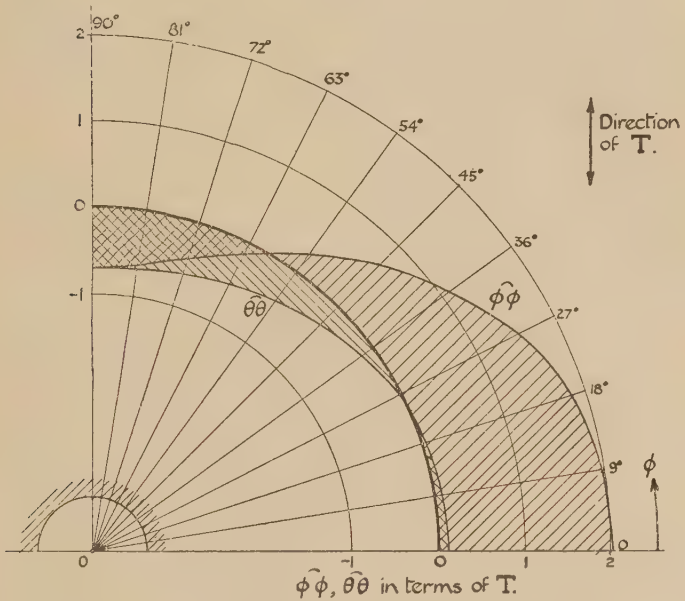
Extension to Compound Stress-Systems. Effect of a Small Spherical Flaw in a Twisted Shaft.

6. The stresses introduced by the flaw upon planes which contain the axis of symmetry are, as we have seen, purely normal. They will be represented by $\widehat{\theta\theta}$, and from fig. 6 can be seen to be of the same sign as T in the neighbourhood of B, and of opposite sign, and in magnitude approximately equal to 2/3T, in the neighbourhood of A.

Suppose, now, that the original stress-system consists of *two* principal stresses, and let us consider the stress-system, in the neighbourhood of the flaw, which corresponds to each separately. The (r, θ) plane for the first system will be a (z, r) plane for the second, and *vice versâ* ; hence, the combined effect on the plane OB (fig. 2) will consist of the $\widehat{zz}$ stresses for the first system, as given in fig. 3, combined with the $\widehat{\theta\theta}$ stresses corresponding to the second system, as given (for points lying on the surface of the flaw) in fig. 6. The second system will increase the stress at some points

of the circular boundary, and will decrease it at others; the resultant effect of two principal stresses which have given magnitudes will evidently be greatest when they have opposite signs.

Fig. 6.

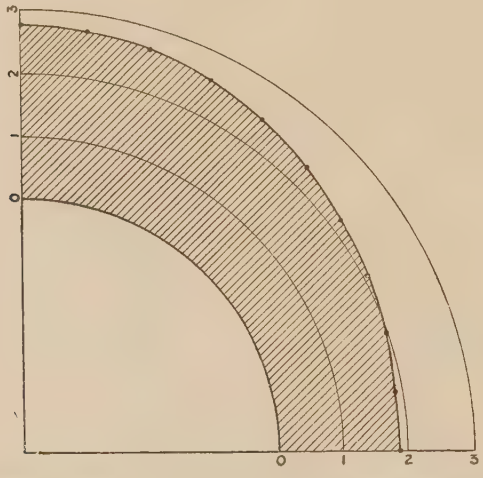


7. Systems which involve *three* principal stresses may be treated similarly; and since the effects of a flaw, in a homogeneous stress-system, are found to be unimportant except in its immediate neighbourhood, we may safely extend our solutions to any elastic system whatever, provided only that the dimensions of the flaw are so far restricted that no appreciable variation in the directions or magnitudes of the principal stresses occurs within a range of (say) three or four diameters from its centre.

For our present purpose it is sufficient to consider the special case of two principal stresses, equal in magnitude and opposite in sign. The results for this case may evidently be employed to investigate the effect of a small spherical flaw upon the stresses which occur in a twisted shaft; for the stress-system which would obtain in the absence of the flaw will here consist at any point of a simple *shear*, of calculable intensity S, and as such can be resolved into two normal stress-components,—a uniform tension of intensity S

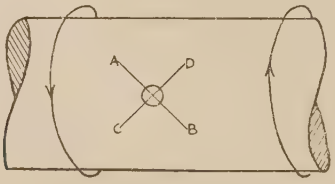
in one direction (making an angle of 45° with the axis of the shaft), and a uniform compression of equal intensity in a direction perpendicular to this. The effects of a spherical flaw on each component system will be of the nature illustrated in figs. 3–6, and the resultant tension on a plane which is perpendicular to the direction of the principal tension will be distributed, at the surface of the flaw, in the manner indicated in fig. 7. The stress is everywhere tensile, and varies slightly with position, its maximum value being of the order 2·7 S.

Fig. 7.



The stress across a plane which is perpendicular to the direction of the principal *compression* will, of course, be similar in magnitude and distribution, but opposite in sign.

Fig. 8.



To sum up:—If a small spherical flaw exists in a shaft which is subjected to torsion, as shown diagrammatically in fig. 8 *, then the stress at the surface of the flaw will range

The flaw is not necessarily situated near the surface of the shaft.

from a maximum tension of about 2·7 S at some point in the plane AB to a maximum compression of the same amount at some point in the plane CD. For points in other planes the stresses will have intermediate values, and detailed investigation shows that the amount of the increase at the surface of the flaw drops fairly quickly as we depart from the planes AB and CD.

Propagation of a Crack in a Twisted Shaft.

8. We may assume that the foregoing results will apply, without serious loss of accuracy, to cases in which the stresses are "alternating,"—*i. e.*, where there is a danger of fracture as a result of fatigue. They are the more important in such cases, in that the power which a ductile material possesses of yielding plastically in regions where the stresses are excessive (thereby equalizing the load) is very much reduced when the stresses are periodic. A fatigue fracture, in fact, exhibits roughly the same characteristics as a fracture in a brittle material ; and if in a crankshaft it originates out of a small flaw in the material, the foregoing considerations suggest that it will spread from the surface of the flaw, as a crack which follows the direction of that surface across which the principal stress is tensile.

Actual materials, as was remarked in § 1, are anisotropic, more especially as regards their resistance to elastic breakdown and to fatigue. At any given point in a crankshaft there will be one or more directions in which cracks will extend more readily than in others, and in general these directions will not coincide with the direction in which, on the foregoing theory, a crack would have extended in an isotropic material. It follows that the direction actually followed by the crack at any point will be a compromise between the direction of least resistance and the direction of greatest effect. But in the material as a whole, if the directions of greatest weakness are arranged at random, without definite orientation, we may still assert, speaking statistically, that the crack will follow the helicoidal surface across which the tensile stress has maximum values, although we shall not be surprised to find that the surface of the fracture exhibits facets which are inclined to its general direction.

Again, if a flaw of spherical shape, which possesses perfect symmetry, concentrates the tensile stresses upon planes of such definite orientation, it is to be expected that the crack will exhibit an even more pronounced tendency to follow a definite direction when once it has started; for the intense

curvature of the free surface at the edge of the crack will magnify to an enormous extent a tensile stress which acts perpendicularly to the general direction of the crack, but it will have practically no effect upon a tensile stress which acts parallel to that direction. Thus a crack which spreads in a direction of greatest weakness will tend in so doing to relieve the concentration of stress at its edge, if that direction differs widely from the direction of fracture which our theory would predict for an isotropic material; but if the two directions are more or less coincident, the concentration of stress will become intense. Similar considerations will apply, with greater or less effect, to any stress-system, and the general conclusion stated in §2 will hold, that *a fatigue fracture, once started, follows the surface on which the greatest principal tensile stress occurs.*

We may conclude, in regard to Prof. Jenkin's "spiral fracture," that when the surface of the fracture is inclined at an angle of approximately 45° to the axis of the shaft, it is attributable to fluctuating torsional stresses; whereas a sensible departure of the surface from this direction will indicate the existence of other contributory causes. In the same way, a fracture which followed a plane surface normal to the axis of the shaft would be diagnosed as due to fluctuations either of axial tension or of flexural action, and so on.

Part II.—The Origin of Fatigue Fractures.

Application of the Theory to Laboratory Tests. Preliminary Experiments.

9. The theory outlined in the preceding paragraphs affords an explanation of the paths which are followed by fatigue fractures once they have started, but it has no direct bearing on the question of their *origin*. On the supposition that the material was initially weakened by a small flaw or by a surface scratch, we have all the conditions which it requires in order to explain an observed "spiral fracture"; and in an example of the kind contemplated by Prof. Jenkin (where some cause of abnormal weakness must be assumed, to account for failure under loads which would ordinarily have been safe) the supposition seems permissible. But to explain the invariable occurrence of spiral fractures when specimens of certain materials are broken under alternating torsion in the laboratory, we must have recourse to some other hypothesis: either discontinuities of structure, equivalent to

ultramicroscopic flaws, must normally exist in these materials even when their quality would be generally regarded as "sound," or the test must have brought about local concentrations of stress which were sufficiently intense to overcome the cohesion of the material.

The first hypothesis has been advanced by A. A. Griffith, in an important paper *, to explain the very low strength of brittle materials in relation to their theoretical "cohesion"; and the arguments by which he supports his theory are so convincing that recourse to the second hypothesis seems unnecessary, so far as brittle materials are concerned. But in the case of certain ductile materials torsional fatigue fractures commonly extend in circumferential or axial directions,—that is to say, along surfaces generally coincident with those of maximum shear and zero tension. On the basis of the first hypothesis, we must account for this different behaviour by assuming that *flaws of the kind contemplated in Griffith's theory of brittle substances do not normally exist in these ductile materials.*

10. To establish the validity of this explanation, it must be shown that ductility will not prevent the occurrence of helicoidal fractures in cases where a flaw is initially present. Torsional fatigue tests were accordingly undertaken on a series of hollow specimens (external diameter 0·400 in., internal diameter 0·313 in., length of parallel portion 1·2 in. and 0·8 in.) cut from two different steels, the carbon content being 0·27 per cent. and 0·65 per cent. respectively. The improved Stromeyer machine † was employed, and the stress cycle was in every case symmetrical about a zero mean value; the ranges of stress which were required to produce fracture of the material are given in the appended table of mechanical properties.

Fractures typical of those obtained in the torsion tests are shown in fig. 9. The specimen numbered 1 was of 0·27 per cent. carbon steel, and fractured circumferentially after 300,000 reversals of a stress cycle ranging between $\pm 8{\cdot}0$ tons/sq. in.; but an exactly similar specimen (No. 2), in which an initial flaw was created by drilling a small hole (0·0125 in. diameter) radially through one side, gave the double helicoidal fracture shown in the photograph. Fracture occurred in this instance after 830,000 reversals of a stress-cycle ranging between

* Phil. Trans. Roy. Soc. A, vol. 221, pp. 163–198 (1920).

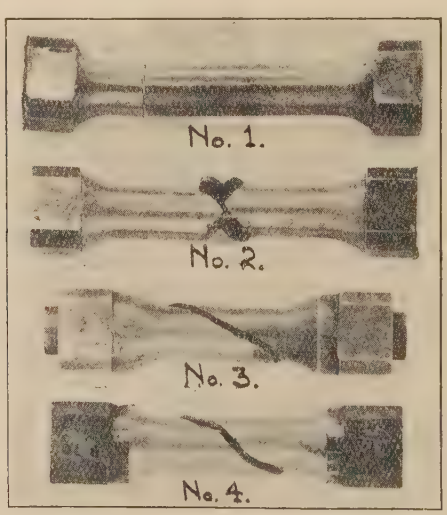
† *Cf.* H. J. Gough, 'Fatigue of Metals' (Scott, Greenwood & Sons, 1924, p. 40).

$\pm$ 7·0 tons/sq.in. (calculated without regard to the effect of the hole).

TABLE I.—Mechanical Properties of 0·27 per cent. and 0·65 per cent. Carbon Steels.

		0·27 per cent. C. Steel.	0·65 per cent. C. Steel.
Static Tensile Tests.	Limit of Proportionality (tons/sq. in.)	20·6	19·2
	Yield Stress „ „	21·0	28·0
	Ultimate Stress „ „	31·2	53·0
	Percentage Elongation at Fracture (on a gauge length of 3·6 diams.) ...	44	19
Fatigue Tests.	Limiting Range of Stress in Reversed Bending Test (tons/sq. in.).....	$\pm$15·2	$\pm$21·0
	Limiting Range of Stress in Reversed Torsion Test (tons/sq. in.)	$\pm$ 7·3	$\pm$10·5

Fig. 9.



The propagation of the crack along *two* helicoidal surfaces concurrently is at first sight surprising. But it will be

realized that in the course of a complete cycle of alternating torsion each of the surfaces in turn is subjected to an intense concentration of tensile stress, while the other experiences a similar concentration of compressive stress ; thus the crack will extend along each surface during the particular half-cycle in which a tensile stress acts across that surface, but will merely be closed (without recovery of cohesion across the fractured surface) during the half-cycle in which the surface is subjected to compression. Fairly exact symmetry in the initial conditions is, of course, required for the occurrence of this phenomenon, in order that the second crack may be started before the first has extended appreciably : it frequently happens that only one surface of separation is formed, as in the case of the specimens numbered 3 and 4 in fig. 9, which were both cut from the harder (0·65 per cent. carbon) steel. The specimen numbered 3 was undrilled, and gave the typical helicoidal fracture after 204,300 reversals of a stress-cycle ranging between $\pm 10{\cdot}8$ tons/sq. in. The specimen numbered 4 was drilled in exactly the same way as No. 2, and broke after 100,000 reversals of a stress-cycle ranging between $\pm 10{\cdot}4$ tons/sq. in. (calculated without regard to the effect of the hole).

11. *In all cases, when a flaw was created by drilling and the specimen then subjected to alternating torsion, helicoidal fractures resulted.* The tests thus appeared to confirm the theory of the present paper, as regards the statistically isotropic materials for which it was propounded; but it seemed desirable to investigate whether this isotropy could be so far destroyed by initial stressing as to make the fracture follow a circumferential or axial path in spite of the existence of a flaw. If, for example, a drilled specimen were given a large initial twist by the application of a steady couple, a sufficient degree of ductility would prevent the occurrence of a helicoidal fracture under this load ; yet it seemed possible that the large amount of slip involved on axial and circumferential surfaces might result in the formation of minute flaws, either within the crystals or (more probably) at the crystal boundaries, and thus leave the material, as it were, "perforated" along these surfaces : if so, the fracture resulting from an alternating torsion cycle might be expected to start at the drilled hole, but to extend through the "perforations" rather than along the helicoidal surface which otherwise would be its natural path.

Further Experiments. The Effects of Initial Straining.

12. To test these ideas, a more systematic series of experiments was initiated. Two steels—one "mild" and one "hard"—were selected, on which many tests of various kinds had already been conducted, and which were therefore known to fracture, when tested in the form of solid specimens under alternating torsion, in very consistent fashion,—the hard steel along helicoidal and the mild along axial or circumferential surfaces. The following table gives properties of these materials which had been obtained previously :—

TABLE II.—Analyses and Mechanical Properties of "A" and "B" Steels.

Steel.	"A" (0·13 per cent. C.)	"B" (0·65 per cent. C.)
Analysis	C 0·13 Si 0·18 Mn 0·70 S 0·042 P 0·046	C 0·65 Si 0·14 Mn 0·11 S 0·20 P 0·03
Heat Treatment	Normalized at 850° C.	As received (hot rolled).
Tensile Test Results :—		
Yield Stress	20·0 tons/inch².	28·0 tons/inch².
Ultimate Strength	30·6 „ „	53·0 „ „
Elongation, per cent. (on length $l = 4\sqrt{A}$, where A = area of cross-section)	40·0	16·0
Contraction of Area, per cent.	71·7	31·8
Wöhler Fatigue Range	16·3 tons/inch² (on 250×10^6 reversals basis).	21·0 tons/inch² (on 20×10^6 reversals basis).
Haigh Machine Fatigue Range	13·8 tons/inch² (on 10^7 reversals basis).	19·2 tons/inch² (on 10^7 reversals basis).
Stromeyer Machine Fatigue Range (Hollow specimens)	8·5 tons/inch² (on 10^7 reversals basis).	10·5 tons/inch² (on 10^7 reversals basis).

Hollow specimens were employed, the dimensions being as follows :—

External Diameter of Specimen	0·400 in.
Internal Diameter of Specimen	0·313 in.
Length of Parallel portion of Specimen.	1·10 in.
Total Length of Specimen	2·70 in.

13. The scheme of the experiments included the following tests :—

(*a*) Static torsion test (single-lever Buckton machine) : the torque-twist curve to fracture was determined. (One specimen of each material.)

(*b*) The typical fracture under a range of reversed torsional stresses was determined. (One specimen of each material *.)

(*c*) A hole (0·013 in. diam.) was drilled through one side of the hollow specimen, and a fatigue fracture obtained. (Two specimens of each material.)

(*d*) The material was subjected to four reversals of static overstrain ; a hole was then drilled (of the same size as before), and the specimen fractured in fatigue. (Two specimens of each material.)

(*e*) The hole was drilled first, and the specimen subjected subsequently to four reversals of static overstrain, followed by a fatigue test to fracture. (Two specimens of each material.)

For the fatigue tests, the improved Stromeyer machine was employed. The ranges of torque applied (which in this machine are conditioned in some degree by the elastic behaviour of the specimen) are given in the following tabular summary of results :—

TABLE III.—Fatigue Tests on the Mild Steel "A" (fig. 10)†.

In the Static Torsion Test (*a*), the specimen (No. AVN5Q) yielded under a torque of 206 inch-lb. (shear stress at yield = 11·7 tons/inch^2), and failed (by collapse, see fig. 10) under a torque of 400 inch-lb. (modulus of rupture = 22·7 tons/inch^2). In the tests (*d*) and (*e*), the static overstrain (preliminary to the fatigue tests) was produced by a torque of ±250 inch-lb. (shear stress = ±14·2 tons/inch^2).

Conditions of Test.	Specimen Number.	Range of Torque (inch-pounds).	Reversals to Fracture.
(*b*)	AVN5N	±16	Less than 1,000,000 (Cut-out did not operate).
(*c*)	AVN5O	±144	Less than 650,000 (dto.)
	AVN5P	±148	244,400
(*d*)	AVN5U	±144	58,400
	AVN5T	±148	113,700
(*e*)	AVN5R	±147	521,000
	AVN5S	±154	298,000

* Including tests made previously, the normal fracture was determined on six specimens of each material. The results were in all cases identical with those given in the tables and diagrams.

† The letters on the specimens in fig. 10 correspond with the final letters of the "Specimen Numbers" (column 2 of Table III).

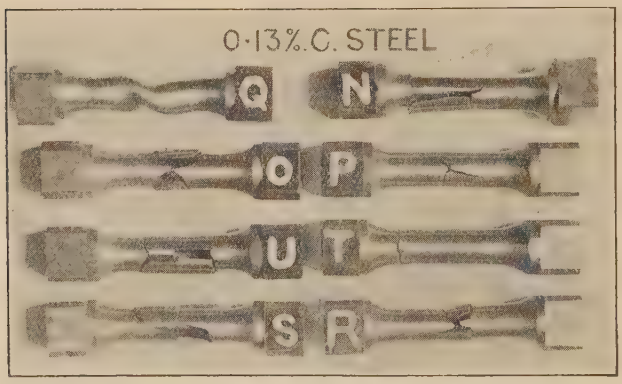
TABLE IV.—Fatigue Tests on the 0·65 per cent. C. Steel "B" (fig. 11)*.

In the Static Torsion Test (*a*), the specimen (No. B.11.F. 2) yielded under a torque of 275 inch-lb. (shear stress at yield = 15·6 tons/inch^2), and failed (by collapse, see fig. 11) at a torque of 700 inch-lb. (modulus of rupture = 39·8 tons/inch^2). In the tests (*d*) and (*e*), the static overstrain (preliminary to the fatigue tests) was produced by four applications of a range of torque of ±375 inch-lb. (shear stress = ±21·3 tons/inch^2).

Conditions of Test.	Specimen Number.	Range of Torque (inch-pounds).	Reversals to Fracture.
(*b*)	B.11.F.1.	±289	94,300
(*c*)	B.11.F.7.	±210	507,800
	B.11.F.8.	±261	12,000
(*d*)	B.11.F.3.	±210	68,200
	B.11.F.4.	±219	9,400
(*e*)	B.11.F.5.	±210	55,100
	B.11.F.6.	±233	6,700

14. The general appearance of the fractured specimens will be seen from the photographs of figs. 10 and 11 ; the

Fig. 10.



actual directions of the fractures are shown more clearly by fig. 12, in which the outer surface of the parallel portion of each fatigue specimen has been developed. Letters and numbers in this drawing conform with those of figs. 10 and 11; the developments have been arranged so that the point at

* The numbers on the specimens in fig. 11 correspond with the final figures of the "Specimen Numbers" (column 2 of Table IV).

which fracture commenced appears at the centre of the developed area.

Fig. 11.

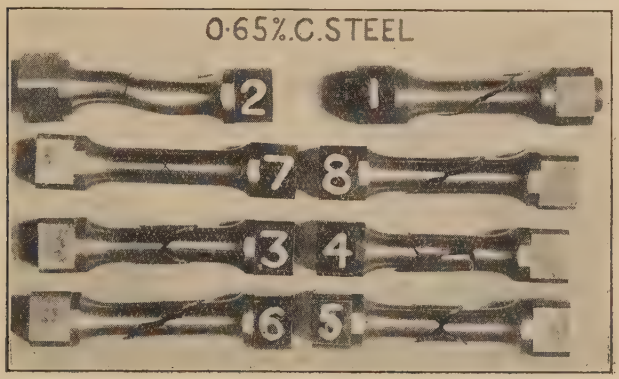
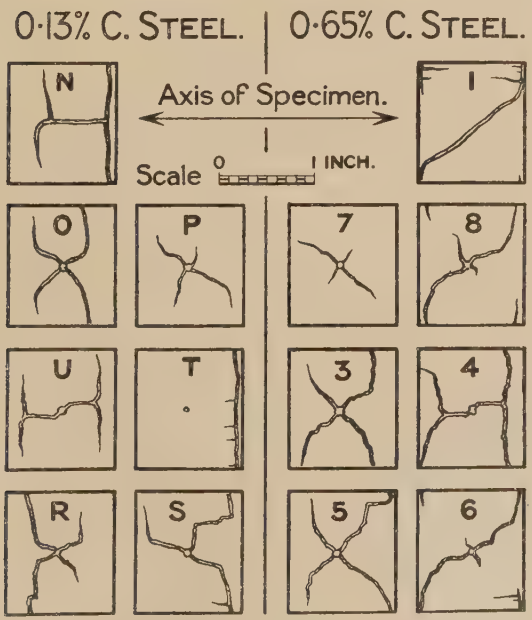


Fig. 12.



Considering the tests in the order given in § 13, we conclude from the type of failure which occurred in the static tests (*a*) that both materials possess a considerable measure

of "ductility"; this is also shown by the tensile test results given in Table II. On the other hand, the typical fractures obtained in the standard torsional fatigue tests (*b*) show that these two materials differ in their behaviour under alternating stresses in the same way as did the materials tested in the preliminary experiments (§ 10). Tests (*c*) on the drilled specimens confirm the conclusion of § 11, that a flaw (at all events, when its size is that of the drilled holes) invariably results in a helicoidal fracture of the statistically isotropic material under alternating torsional stresses.

Initial overstrain, applied to the specimens before drilling, is shown by tests (*d*) to have such important effects on the "A" material that one specimen (No. AVN5T, fig. 12) fractured circumferentially along a surface which did not pass through the drilled hole. In the "B" material also it has a perceptible tendency to make the fracture follow an axial or circumferential path, but the causes making for helicoidal fractures are here less definitely outweighed. Tests (*d*) indicate that the effect of overstrain is reduced when the hole is drilled first; but it is still perceptible.

General Conclusions.

15. It has been remarked already (§ 9) that no light is thrown by the theory of Part I upon the *origin* of fatigue fractures; neither is it claimed that the experiments just described have gone far to supply an explanation. More and more it appears that the phenomena of fatigue in metals are intimately related with their molecular structure, and will not be explained by a mere elaboration of mechanical tests on the crystalline aggregate. But one fact may fairly be regarded as established by the present investigation,—that a flaw in statistically isotropic material inevitably results in the helicoidal type of fracture under alternating torsional stresses; and this being so, something may perhaps be learned from a study of the experimental fractures as indicators of the existence or non-existence of "flaws",—more especially if we can avoid reference to controversial questions which are involved in particular theories of breakdown and fatigue.

In a material like cast iron, which fractures along a helicoidal surface even when tested under static torsion, we may conceive, as in Griffith's theory *, that "flaws" (*i. e.*, cavities large enough to be tractable by the mathematical theory of

* *Loc. cit.*, pp. 179, 193.

Part I) are initially present, and that these, owing to its low ductility, produce local concentrations of stress which result in rupture of the material. So far as our experience goes, no other metal which is commonly employed in engineering behaves in this way: in the "B" steel of §§ 12–14, for example, the typical fracture under static torsion is illustrated by the specimen numbered 2 in fig. 11. The reason presumably is, not that the material in its normal condition has no flaws, but that high intensification of stress under static loading is prevented by its ductility; for the invariable occurrence of helicoidal fractures in the normal fatigue tests (*b*), where the ductility was less able to relieve the stress-concentration, indicates that flaws were certainly present at an early stage in the tests, and that they have had the result which our theory would predict.

This view is confirmed by the very distinct types of fracture obtained with the "A" and "B" steels in tests (*b*), which suggest that flaws were present in the "B" material, but not in "A". Thus we have indications of a difference between the "A" and "B" materials which is something more than a mere difference in respect of the property known as "ductility"; we may describe it by saying that the "A" material offers greater resistance to the formation of flaws in the course of manufacture or of mechanical treatment such as "cold-work,"—a quality which it is perhaps permissible to term "gumminess." No evidence is available, of course, from our mechanical tests to indicate whether surface tension is, in fact, a measure of the quality.

16. If in the "B" steel flaws were present initially, "perforation" of the material, which in § 11 was contemplated as a possible result of overstrain, might be expected to have a somewhat indefinite influence on the direction followed by a subsequent fatigue fracture; this we have seen (§ 14) to be the case. But it remains an open question whether the action of overstrain is, in fact, described by the notion of "perforation"; and even though this description were true of the "B," it would not necessarily be true of the "A" material. *The most significant result of the tests is the axial or circumferential direction followed by a normal fracture of the "A" steel**; for it must be remembered that the crack has extended gradually, and according to the theory of Part I it should have an overwhelming tendency to follow a

* Fractures following these directions are fairly typical of high-grade mild steel: mild steel of indifferent quality often gives a helicoidal fracture.

helicoidal path when once it has started. Thus it seems certain that the slipping on axial and circumferential surfaces, which occurs from the beginning of a fatigue test, has in some way destroyed the statistical isotropy of the material and caused these surfaces to become directions of special weakness ; but it seems equally clear that the weakness must be due to a modification of the material rather than to the formation of flaws, since *the directions of special weakness must have been established by the time that the first flaw was formed* ; and if this modification is the result of the to-and-fro slipping which occurred in tests (*b*), it is conceivable that the slipping which occurred in tests (*d*) under the initial static overstrain had a similar effect.

17. The general conclusion would appear to be, that the direction followed by a fatigue fracture, in a laboratory test of undrilled material, is influenced by two factors,—the tendency of a crack to intensify stress, and the tendency of slipping on any surface of the material to make this a direction of special weakness. The tendency of the crack has been shown, both by theory and experiment, to be development along surfaces of maximum *tension* (*i. e.*, in a torsion test, along helicoidal surfaces) : the tendency of the slipping is to make the crack follow surfaces of maximum *shear*,—*i. e.*, surfaces inclined at 45° to the first. Either tendency may predominate under suitable circumstances, and the balance may be so nearly even, in special instances, that both effects are perceptible in turn. Thus it is frequently noticed, in testing specimens which increase in diameter towards their ends by a continuous transition curve, that a fracture which starts in an axial direction branches off into helicoidal paths as this curve is approached : presumably the explanation is, that the shear imposed by the initial overstrain decreases with the increase in diameter, so reducing the amount of the slipping, and hence the degree of weakness produced, in axial and circumferential directions ; the "flaw effect" then predominates, and controls the subsequent path of the fracture.

Of the two conflicting factors just mentioned, the present paper, being in the main theoretical, really deals only with one,—the effect of flaws after their initiation. But in regard to the second—the weakening effect upon the crystalline aggregate—it suggests two important conclusions : first, that the weakening is probably not described by the notion of "perforation,"—*i. e.*, that it is due to something other than the formation of large numbers of flaws along the

surfaces of maximum slip ; and secondly, that this other process, whatever it may be, is almost certainly a precursor of the fracture, and therefore predominant in importance for the problem of fatigue. The study of fractures is of value in the diagnosis of failures which have occurred in practice ; but the outstanding question in the general problem is the nature of the process (possibly a modification of molecular structure) whereby surfaces on which continued slipping has occurred are made directions of special weakness, although no discontinuity, such as is suggested by the term "flaw," is brought into existence.

VII. *The Absorption of Hydrogen in Potassium Vapour Arcs.* *By* Rogers D. Rusk, *Ph.D., Ryerson Physical Laboratory, University of Chicago* *.

IT has been noted by Gehlhoff † and others that hydrogen is rapidly absorbed by hot potassium vapour when a high-tension electric discharge is passed through the vapour. In the following experiments the absorption was found to occur in a low voltage arc in which ionization currents were obtained between a coated platinum filament and an anode, through hot potassium vapour and hydrogen.

Hydrogen and potassium combine chemically to form potassium hydride ‡, KH, when they are heated together, and most probably the combination occurs in the presence of atomic hydrogen. The dissociation of hydrogen in an electric arc may be due to electron impacts, to thermal effects, or to the impacts of ions or excited atoms or molecules. If we take the heat of dissociation of a gram-molecule of hydrogen to be 84,000 calories, as given by Langmuir, the required energy per molecule is 3·6 volts. It might be suspected that direct electron impacts of this amount would produce dissociation, but Hughes § has made a very careful investigation and has found no trace of such dissociation due to impacts of less than 13 volts energy, and only slight dissociation below 16 volts. The question arises as to whether or not there is a critical potential for dissociation that would be indicated by the combination of H with K.

* Communicated by Prof. A. J. Dempster.
† *Verh. d. Deutsche Phys. Ges.* xiii. p. 271 (1911).
‡ Moissan, *Compt. Rend.* cxxxiv. p. 71 (1902).
§ Phil. Mag. xli. p. 778 (1921).

Horton and Davies * have found that the radiation at 11·9 volts is handed on to shielded electrodes by the molecules, while that at 12·9 volts is not. This, they suggest, indicates that the 12·9 volt radiation is due to dissociation of the molecules and resonance of the atoms. This would account for the lower limit of dissociation given by Hughes, except that the work of dissociation (12·9 volts − 10·3 volts) comes out only 2·6 volts.

Hughes estimates that at 140 volts approximately every collision produces dissociation. The dissociation he obtained at 13 volts was very slight and approximately one-tenth that at 16 volts, so that at or near 16 volts a sharp increase in the absorption occurred. This would be in agreement with the interpretation that has been usually given to the 16 volt level, as the one at which dissociation plus ionization of one of the atoms occurs.

Olmstead †, in studying radiation and ionization effects, was able to assign definite critical potentials to molecular hydrogen, but without determining whether or not there was dissociation. Duffendack ‡ found that the Balmer series appears at 16 volts, and this observation, which was confirmed by Horton and Davies, was taken to indicate dissociation plus ionization of one of the atoms.

The dissociation and formation of the charged atom probably occur, however, as a result of a secondary process. Dempster § has shown by a positive ray analysis of the products of ionization that the presence or absence of hydrogen atoms and H_3, when hydrogen is ionized by electron impacts, is determined by the pressure in the tube. Hydrogen atoms were not formed at all as a primary effect with electrons of the velocity used, but only singly charged molecules. When the pressure was high enough to allow collisions to occur, charged atoms and the complex H_3 were formed. Probably some of the molecules were thrown into excited states with energy sufficient to produce dissociation and ionization upon collision ‖. Smyth ¶ has recently used similar methods in analysing the products of ionization produced by electrons of various voltages. In his paper in the 'Proceedings of the Royal Society,' he concluded that

* *Ibid.* xlvi. p. 872 (1923).
† Phys. Rev. xx. p. 613 (1922).
‡ Phys. Rev. xx. p. 665 (1922).
§ Phil. Mag. xxxi. p. 438 (1916); Phys. Rev. viii. p. 651 (1916).
‖ J. Franck, *Ergebnisse der Exakte Naturwissenschaften*, ii. p. 107.
¶ Proc. Roy. Soc. 105 A, p. 119 (1923): Jr. Frank. Inst. cxcviii. p. 795 (1924).

there were different critical minima potentials in hydrogen, 20·2 volts for the formation of charged hydrogen atoms and 16 volts for charged hydrogen molecules. Hogness and Lunn * have also examined the products formed by low voltage electrons, and find values of 15·7 volts for the formation of the charged hydrogen molecule and 16·6 volts for the charged hydrogen atom. Recently Smyth † has ascribed his former result to an insufficient consideration of the effect of the gas-pressure on the products present, and finds that charged atoms as well as molecules may be present with electron impacts of about 16 volts. The slight difference in Hogness and Lunn's experiments may possibly be due to experimental uncertainties in the corrections applied.

That hydrogen may be dissociated by collisions with mercury atoms excited by 2537 Å. radiation, which is equivalent to an energy of 4·9 volts, has been shown by Franck and Cario ‡, who illuminated a mixture of hydrogen and mercury vapour with the 2537 Å. radiation from a mercury arc, and observed the change in pressure of the hydrogen. The atomic hydrogen produced was condensed on cold walls, or oxidized by copper oxide, and the resultant water vapour frozen out. The same effect has been studied in a low voltage arc by Compton and Duffendack §. Since the energy of excitation of the mercury is just greater than the energy of dissociation of the hydrogen, the resultant dissociation is in agreement with the theory of Klein and Rosseland ‖. With hydrogen in potassium vapour such dissociation due to collisions with excited potassium atoms in the first excited state would not be expected, since the first resonance potential of potassium is 1·6 volts. However, as the ionizing potential of potassium is 4·3 volts, we might have the interchange of energy from some of the higher excited states to the hydrogen molecule.

Experimental.

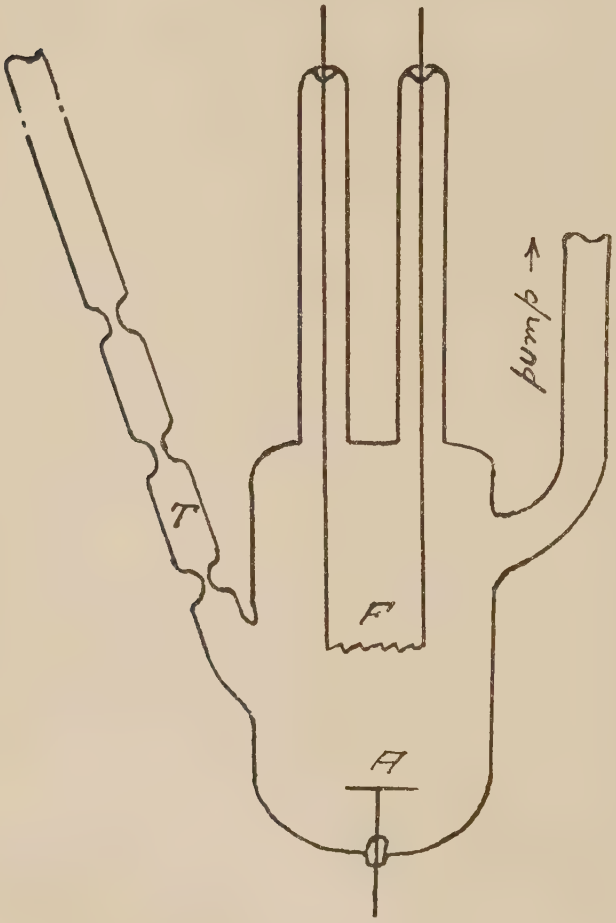
With pressures in the neighbourhood of one millimetre of mercury, absorption of hydrogen due to the arc was obtained at arc potentials above 16 volts and temperature up to 200° C. Absorption at slower rates was obtained in the presence of the hot filament alone, while at higher

* Proc. Nat. Acad. Sc. x. p. 398 (1924).
† Phys. Rev. xxv. p. 452 (1925).
‡ *Zeit. f. Phys.* xi. p. 161 (1922).
§ Phys. Rev. xxiii. p. 583 (1924).
‖ *Zeit. f. Phys.* iv. p. 46 (1921).

temperatures and pressures absorption was obtained by simply heating the hydrogen and potassium together.

The experimental tube, one form of which is shown in

Fig. 1.



The Experimental Tube.

fig. 1, contained a coated platinum filament, F, a nickel anode, A, and a side tube, T, with constrictions for filling with potassium. The rate of absorption of the hydrogen was obtained from observations of the change in pressure,

made in the usual manner with a McLeod gauge. A liquid air-trap took out water-vapour and mercury, and the system was evacuated by a mercury-vapour pump. A stop-cock enabled the experimental tube and McLeod gauge to be isolated from the rest of the system while a series of observations was being made.

Caution was observed in filling with potassium in order to have it as pure as possible. A coating on the surface of the potassium greatly reduced the absorption, and it was noticed that a straight chemical absorption occurred if any oxygen was present. Hence traces of air or water-vapour were particularly undesirable. The procedure was first to pump down the tube and bake out the residual gas at 400° C. The filament was out-gassed for several hours at a higher temperature than that at which it was to be normally run. The potassium was introduced into the filling-tube and partially distilled by repeated melting down and sealing off the residue *in vacuo* or in an atmosphere of hydrogen. The temperature of the tube was then controlled by a heating-coil placed around the tube. Pressures of the hydrogen were read every one, two, or three minutes, first with the arc and filament off, next for a few minutes with the arc off but with the filament on, and finally with the arc on.

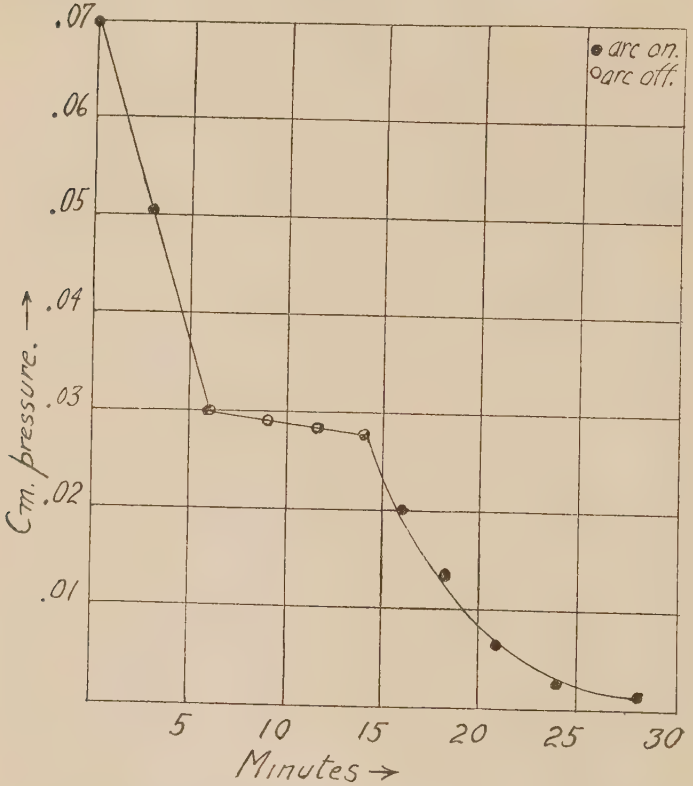
Arc currents up to 30 milliamperes were obtained, and the filament current was continually adjusted as the pressure went down in order to keep the filament temperature as nearly constant as possible. It was found that the absorption of the hydrogen due to the thermal effect of the filament was appreciable at temperatures above a very dark red, and increased rapidly with the temperature Hence the filament was burned at as low a temperature as possible. In calculating rates of absorption, corrections were applied for the effect of the filament when it was not negligible. Any absorption on cold walls, as in the experiments of Hughes, and Franck and Cario, was of course not present, due to the high temperature of the tube.

On account of the experimental difficulties involved, it was found impossible to control all factors in such a way as to obtain exactly the same rate of absorption for successive experiments, though the results were in general qualitative agreement. The absorption of the hydrogen was usually accompanied by a characteristic violet colour of the arc, while at lower voltages a green colour predominated, and no absorption occurred.

Data and Results.

Figs. 2 and 3 give the observations in typical experiments. It is noted that the absorption is rapid at the start, and that sharp breaks occur in the curve where the arc was temporarily cut off. The smaller absorption here was due to the thermal effect of the hot filament. The study of a large

Fig. 2.



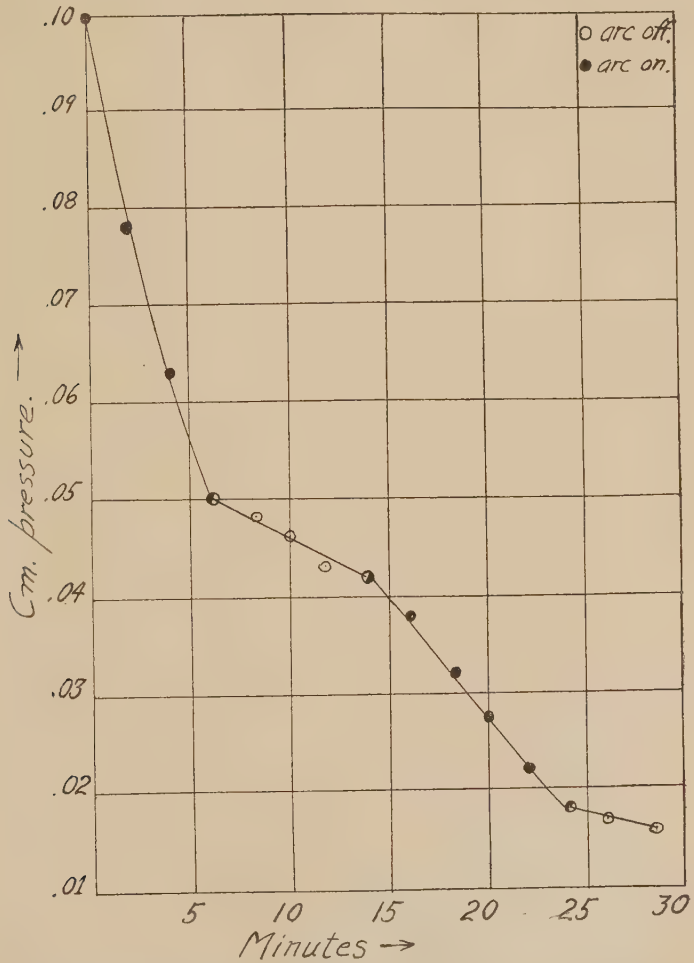
Typical Absorption-Curve, 190° C., 22 volts, 30 milliamperes.

number of such curves indicates that during the early part of each experiment the time rate of pressure change, $\frac{dp}{dt}$, was steady, and that it then decreased and finally decayed to the dissociation pressure of the potassium hydride.

The vapour-pressure of the potassium being small, in

comparison with the pressure of the hydrogen, the arcs were mainly arcs in hydrogen, except at extremely low pressures of the hydrogen. The striking voltage of the arc varied with the temperature, but the arc could always be struck at the ionization potential of the hydrogen.

Fig. 3.

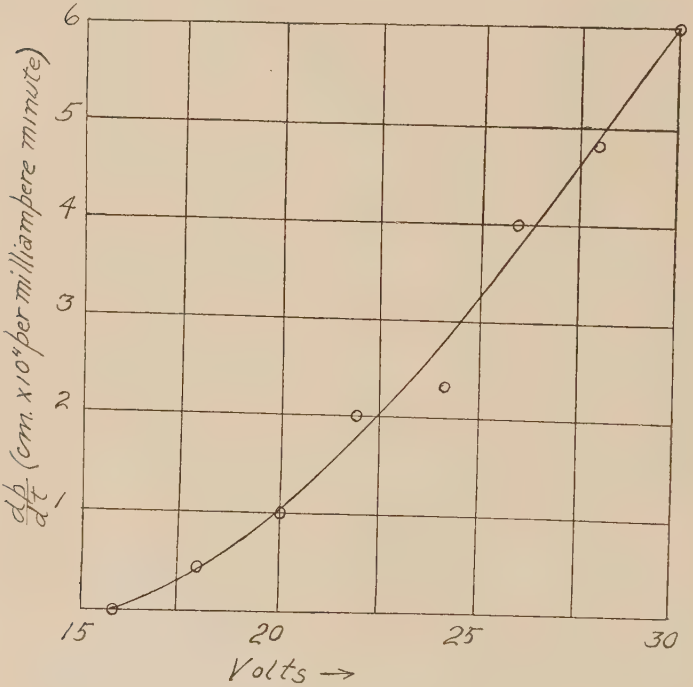


Typical Absorption-Curve, 190° C., 28 volts, 17·5 milliamperes.

With suitable vapour densities of the potassium it could be struck much lower, and was struck as low as 6 volts, but at the higher temperatures dissociation of the potassium

hydride was appreciable. Between 16 and 22 volts the arc was particularly unstable and sensitive to temperature fluctuations. As the absorption progressed the filament temperature would rise, resulting in greater electron emission and consequent lower voltage drop across the arc. Further absorption would reduce the ionization of the hydrogen and decrease the conductivity of the arc, resulting in an increased potential drop. The addition of a high resistance in the arc circuit helped to stabilize it.

Fig. 4.



Rates of Absorption at different Potentials.

Fig. 4 represents the results obtained with one tube, with which several series of observations were made. The ordinates give the rate of pressure decrease at the beginning of a series of observations for pressure in the neighbourhood of 1 mm. The rate of absorption increases rapidly with increasing voltage across the arc. Below 16 volts no absorption due to the action of the arc could be detected. Such an absorption, if present, was certainly less than

·0001 mm. per milliampere-minute, and was probably less than one-fifth that, as compared with ·002 mm. observed at 22 volts. Previously noted traces of absorption * below 16 volts are attributed to the presence of a slight amount of oxide or dissociation by the filament.

Gehlhoff † mentions that "complete absorption" occurs at 190° C. At this temperature it was found that the absorption was most rapid, and dissociation of the potassium hydride was small. Keyes ‡ has measured actual dissociation pressures of potassium hydride between 215° C. and 415° C., and he gives the following formula for the dissociation pressure :—

$$\log p = -\frac{5850}{T} + 2{\cdot}6 \log T + 3{\cdot}895.$$

At 190° C. the dissociation pressure is ·001 cm. However, the absorption was obtained with lower temperatures, although at slower rate, as shown in fig. 5. Here the arc potential was 180 volts and the dissociation by the filament was negligible, due to the low temperature at which it was burned. It was found that the absorption was roughly proportional to the vapour density of the potassium. Dushman § gives an extrapolated value of $6{\cdot}84 \times 10^{-10}$ mm. for the dissociation pressure of KH at 27° C. To this theoretical residual pressure the hydrogen should be cleaned up at that temperature, but the rate of clean-up would be extremely slow.

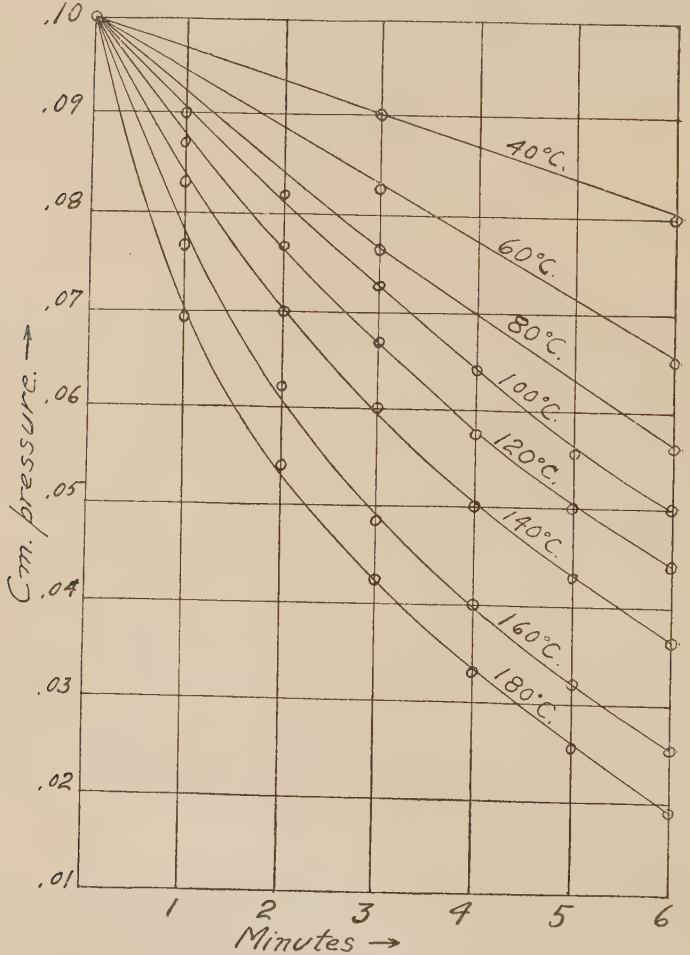
The dissociation pressure of potassium hydride rises rapidly with increased temperature. It was found that an increase of the temperature of the tube, even while the arc was running, could be made to produce dissociation which, depending upon the amount of hydride present, would decrease the net absorption or cause a reversal with evolution of hydrogen and rising pressure. After absorption, and with the arc off, the hydrogen could be restored by raising the temperature of the tube.

For a comparative test, mercury-vapour was introduced into the arc with the hydrogen and potassium, and absorption at potentials below 16 volts was immediately observed, together with the appearance of the mercury lines in the arc. At 13 volts across the arc the absorption in the presence of the mercury was of the same magnitude as that at

* Phys. Rev. xxi. p. 720 (1923).
† *Loc cit.*
‡ J. Am. Chem. Soc. xxxiv. p. 779 (1912).
§ "High Vacua," General Electric Review.

22 volts without the mercury. This is direct evidence, as Franck and Cario * have shown, that energy may be transferred to the hydrogen by means of collisions of the

Fig. 5.



Absorption at different Temperatures, 200 volts, 3 milliamperes.

"second type," and that the energy of excitation of the mercury is capable of dissociating the hydrogen in a manner not possible by direct electron impacts of the same energy.

* *Loc. cit.*

Using an ordinary glass tube without filament or electrodes, the absorption was measured at atmospheric pressure due to temperature alone. At 300° C. the absorption was ·2 c.c. per hour, and at 375° C. it was 4·8 c.c. per hour. Thus it appeared that the phenomena of the absorption produced in the arc could be reproduced, in effect at least, without the arc by sufficiently raising the temperature, an increased pressure of the hydrogen, of course, being necessary on account of the increased dissociation pressure of the potassium hydride.

Discussion and Conclusions.

The absorption in the arc is evidently due to some active type of hydrogen which is not formed at less than 16 volts. Ionized potassium does not unite with molecular hydrogen, otherwise absorption would have occurred at 4·3 volts, the ionization potential of the potassium.

The active form of hydrogen present in the arc may be the charged hydrogen molecule, which might combine directly with a K-atom, freeing one of the H-atoms. But from experiments discussed in the introduction, it seems more probable that hydrogen atoms are formed as the result of a secondary process whenever charged hydrogen molecules are present. We may then suppose the combination to take place between potassium atoms and hydrogen atoms. On this view 16 volts is the lower limit at which dissociation of the hydrogen occurs.

The negative chemical characteristics of atomic hydrogen are well known. Bardwell * has shown that hydrogen, in combination with potassium, behaves as a halogen and upon being electrolysed appears at the anode carrying a negative charge. When in union with the potassium atom, the valence electron of the latter doubtless goes to complete, in the hydrogen, the group of two electrons common to the more stable helium form. There is little doubt but that atomic hydrogen, if present in the arc below 16 volts, would readily unite with the potassium.

An upper limit for the rate of absorption in the arc due to the presence of molecular hydrogen ions may be obtained if we assume that all the current is carried by the electrons, and that each electron removed from the arc leaves a positive ion behind. It may be assumed that this positive ion gives rise to an atom which is absorbed by the potassium. At the pressures involved, the fraction of current actually carried

* J. Am. Chem. Soc. xliv. p. 2499 (1922).

by the positives must be relatively small. With one milliampere of current through the arc, $ne = \cdot 0001$ in C.G.S. units, whence $n = \cdot 63 \times 10^{16}$. On the above assumption, n positive molecular ions per second are formed in the arc, and if each gives rise to an atom which is absorbed, or if the molecular ions themselves react with the potassium, then n atoms of hydrogen would disappear per second, or half that number ($\cdot 315 \times 10^{16}$) of molecules would disappear per second.

At 22 volts the observed number of hydrogen molecules disappearing per second per milliampere of current was $\cdot 021 \times 10^{16}$, which is one-fifteenth of the above upper limit. This may be taken to indicate that the molecular ions do not react as fast as they are formed, and that more probably only the atoms formed by a secondary process are absorbed. The figures would then indicate the effectiveness of the secondary process.

The steady rate of change of pressure, $\frac{dp}{dt}$, of the hydrogen which was observed at the start of each run would be expected if the vapour density of the potassium were constant, and if the arc furnished active hydrogen at a constant rate. The absorption was found to be proportional to the current through the arc, except in the case of very intense arcs, in which case there was some evidence of more rapid absorption, which may have been due in part to a higher effective temperature in the arc itself.

If we consider the absorption of hydrogen at high temperatures due to heat alone, the question arises as to whether it is an ordinary chemical reaction between the potassium and molecular hydrogen, or whether it may not be due to atomic hydrogen existing in equilibrium with the latter. The determination of so small an amount of dissociation cannot be exact, but by using Nernst's equation of the reaction isobar given below, the per cent. of dissociation at various temperatures and pressures may be calculated, where x is the fraction of monatomic molecules present.

$$\log \frac{x^2}{1-x^2} P = \frac{-Q_0}{4 \cdot 571 . T} + 1 \cdot 75 \log T - \frac{\beta}{4 \cdot 571} T + \Sigma \nu c \text{ *}.$$

At 300° C. and 76 cm. the per cent. of dissociation is, by the formula, $1 \cdot 75 \times 10^{-11}$. Such a value is a somewhat

* Ehrenfest and Trkal, *K. Akad. Amsterdam, Proc.* xxiii. 1, p. 162 (1920).

extreme extrapolation of the formula, and yet comes surprisingly close to accounting for the observed absorption. If the number of hydrogen molecules in 150 c.c. at 300° C., 76 cm. be taken as $1{\cdot}84 \times 10^{21}$, the number which are monatomic is seen to be $3{\cdot}42 \times 10^{8}$. On the simple kinetic theory each molecule experiences $7{\cdot}77 \times 10^{9}$ collisions per sec. Hence all the hydrogen atoms make $2{\cdot}66 \times 10^{18}$ collisions per sec., of which the fraction $\frac{{\cdot}00497}{76}$, or $1{\cdot}74 \times 10^{14}$, is with potassium atoms, the vapour pressure of the potassium being ·00497 cm., from the work of Keyes*. Assuming that combination occurs at each collision, this would account for the removal of $\cdot 87 \times 10^{14}$ hydrogen molecules per sec., which was about one-sixteenth of the observed rate. If the absorption is due to dissociated hydrogen these figures would indicate the probable magnitude of the dissociation. It is interesting to note that the above value for the dissociation by Nernst's formula is in striking contrast to that given by Langmuir †. The value taken from his table for the partial pressure of dissociated hydrogen, at 500° K. and atmospheric pressure, being $1{\cdot}7 \times 10^{-25}$.

In conclusion, it was found that active hydrogen capable of combining with potassium is found in low voltage arcs above 16 volts; that the atomic form is probably atomic; that the dissociation is most probably due to secondary collisions; and that this dissociation does not occur below 16 volts.

The writer wishes in particular to thank Prof. A. J. Dempster, who suggested the problem, for his continued interest and advice.

VIII. *The Adsorption of Gases by Activated Charcoal at Very Low Pressures.*—I. *At Air Temperature.* *By* H. Rowe, *B.Sc., Demonstrator in Physics, University College of the South-West of England, Exeter* ‡.

1. Introduction.

ALTHOUGH much research has been made on the occlusion and retaining of gases and vapours by different substances, the intermingling phenomena which constitute sorption have not been experimentally identified, but in general there are three actions.

* *Loc. cit.*

† J. Am. Chem. Soc. xxxiv. p. 877 (1912).

‡ Communicated by Prof. F. H. Newman, D.Sc., A.R.C.Sc.

1. Absorption. This is true solution in a solid and obeys Fick's law of diffusion, which requires that it should commence with a very high velocity for the first few moments, but fall off rapidly with time and, theoretically, should require an infinite period for perfect equilibrium to be attained. The action is accelerated by a rise in temperature.

2. Adsorption. This effect is condensation on a surface, and is practically instantaneous. Any time-lag which occurs is explained at present by the interval required for the dissipation of the heat evolved, or by the comparative inaccessibility of the surface on which condensation occurs. Adsorption decreases rapidly with rise in temperature, and it is conditioned by the surface extent, which in the case of metals is small. It is essentially a surface-tension phenomenon, and is sometimes influenced by electro-capillary effects.

3. Chemical reactions. These occur frequently in sorption processes, and may be of decisive importance, *e. g.* the behaviour of catalysts. Where pure chemical compounds are formed, each exhibits a definite decomposition pressure, below which the compound is not produced, and at which formation is complete. Chemical reactions are often present in the most varied phenomena, particularly as such reactions proceed vigorously in surface films, as well as in solid solution.

In 1909 Freundlich * suggested that the relation between the pressure p and the quantity of gas q absorbed might be represented by an equation of the form

$$q = kp^{\frac{1}{n}}.$$

For low pressures or high temperatures, where the quantities adsorbed are small, the value of $\frac{1}{n}$ approaches unity, while at high pressures and low temperatures it often becomes as small as 0·1. These values have been verified experimentally by Claude † and Titoff ‡. They found that in the case of hydrogen $\frac{1}{n}$ is approximately equal to unity at all pressures and temperatures. On the other hand, in the case of nitrogen and carbon dioxide $\frac{1}{n}$ decreases rapidly as the pressure and

* 'Kapillarchemie,' Leipzig (1909).
† *Comp. Rend.* vol. clviii. p. 861 (1914).
‡ *Zeits. Phys. Chem.* vol. lxxiv. p. 641 (1910).

temperature both increase. On the whole the relation does not agree with experimental observations over large ranges of pressures.

Quite recently A. M. Williams* from the kinetic theory of gases has derived relations between the pressure, the quantity of gas adsorbed, and the temperature, which may be expressed by

$$\log q \cdot \frac{R.T.}{p} = B + \frac{A}{T}$$

and

$$\log q \cdot \frac{R.T.}{p} = A_0 - A_1 q.$$

The latter, representing the adsorption isotherm, may also be written in the form

$$\frac{q}{p} = K\epsilon^{-A_1 q}$$

where A_0, A_1, and K are constants at any given temperature. It will be observed that for small values of q, i. e. for small amounts of adsorption, the exponential term is practically unity, so that at low pressures and high temperatures the latter equation reduces to the simple form

$$q = kp.$$

These equations are found to agree well with the experimental results obtained by Claude and Titoff, and also with those of Miss I. F. Homfray †.

According to Langmuir ‡ adsorption is the result of a kinetic equilibrium between the rate of condensation and that of evaporation. On this basis the quantitative form of the adsorption isotherm depends on the nature of the mechanism of both condensation and evaporation. Using these conceptions of surface actions, Henry § has developed a theory which he states applies to all cases where the adsorbent only contains not more than 30 per cent. of the saturation value of the adsorbate. The type of equation obtained is similar to that of Williams, and is

$$\log \frac{\alpha}{p} = \log A - A_1 \alpha.$$

where α is the number of gram molecules adsorbed at the

* Proc. Roy. Soc. (Edin.) vol. xxxix. p. 49 (1919); Proc. Roy. Soc. (Lond.), A, vol. xcvi. p. 287 (1919).

† *Zeits. Phys. Chem.* vol. lxxiv. p. 129 (1910).

‡ Journ. Amer. Chem. Soc. vol. xl. p. 1361 (1918).

§ Phil. Mag. vol. xliv. p. p. 689 (1922).

pressure p; or, reducing the above equation to cubic centimetres of gas at N.T.P., we have

$$\log \frac{q}{p} = A_0 - A_1 q.$$

Most of the investigations on adsorption phenomena have been carried out at pressures above 1 mm. * and at liquid-air temperature, and little is known about adsorption at low pressures and higher temperatures, so that the formula quoted above cannot be compared with experimental results. Claude †, however, has measured the adsorption of various gases at pressures below 10^{-3} mm.

From the known adsorptive capacity of an absorbent at higher pressures and low temperatures, it is not possible to predict with certainty the behaviour at low pressures and higher temperatures, since in the former case, where most gases are near their condensation state, the attraction between molecules of the gas is greater than the molecular attraction between the gas molecules and those at the surface of the solid. The contrary is true, however, at very low pressures, and more especially at higher temperatures.

The amount of gas which charcoal adsorbs and retains varies greatly with the equilibrium pressure; and since the function of charcoal in producing high vacua is the retention within it of gas molecules, it is the adsorption at low pressures which is important. Owing to the difference between the characteristics of adsorption at high and low pressures, it is impossible to predict the rate of adsorption in high vacua, and data given at ordinary pressures bear no relation to the retentivity of the substances at low pressures.

As a study of adsorption phenomena at very low pressures is likely to yield important results concerning the nature of chemical and physical action, a detailed study of the amounts of various gases adsorbed by activated coconut charcoal within the pressure range 10^{-4} to 10^{-1} mm. and at air temperature was made, and empirical relations between the pressure and the volume so adsorbed deduced.

2. *Experimental Arrangement.*

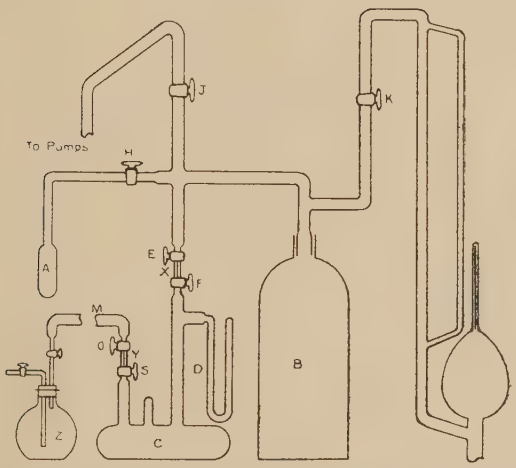
The apparatus used is shown in fig. 1, and consisted essentially of a bulb A containing the activated coconut charcoal which, by means of a tap H, communicated with a large volume B. C, a drying bulb containing phosphorus

* Pressures are expressed in mm. of mercury.

† *Loc. cit.*

pentoxide, was used as a small reservoir, and X and Y were known volumes enclosed between taps. These volumes had been carefully calibrated previously. A sealed-limb mercury manometer D gave an indication of the pressure and hence the amount of gas in the reservoir C. The whole system could be evacuated by means of a Volmer mercury diffusion pump supported by a Cenco-Hyvac oil-pump. All pressures on the high vacuum side of the apparatus were read on a 500 c.c. McLeod gauge, which, having received continuous and prolonged heat treatment and having been in constant use for a considerable time, read consistently and accurately.

Fig. 1.



The gauge was sensitive down to 10^{-5} mm., but the mercury pump when in action exhausted the whole system to a pressure not readable on the gauge. The volume enclosed between the taps J, H, E and the mercury in the McLeod gauge is termed the high vacuum side of the apparatus in the experiments described.

The whole system was evacuated without any charcoal in A to less than 10^{-5} mm., and maintained at this degree of vacuum for several days, the pumps working continuously to remove gases and vapours from the glass walls. After all the gases and vapours had been removed, as indicated by no increase in pressure during an interval of 48 hours while the pumps were shut off, tap F was closed, and by admitting known volumes of dry air from Y into C, the latter was filled with dry air at about 50 mm. pressure.

To determine the volume V of the high vacuum side with which the charcoal tube communicated in all subsequent adsorption readings, the taps J, E, F being closed and H and K open, the pressure of any gas in the system was measured on the McLeod gauge. A known volume v of air at a pressure p indicated by the manometer D was then admitted by opening F, then closing it and opening the tap E. The final pressure after admitting the gas was noted on the gauge, and from these readings the volume V could be calculated.

Let

p_1 = original pressure,

p_2 = final pressure.

Then

$$p_2(V+v)=p_1V+pv,$$

i.e.

$$V=v\frac{(p-p_2)}{p_2-p_1}.$$

p is of the order of several millimetres and p_2 is of the order 10^{-3} mm., so that approximately

$$V=\frac{pv}{p_2-p_1}.$$

This process repeated about 50 times gave the average value of v, which was 3160 c.c.

The volume of the reservoir C was determined in a similar manner, known volumes of air at atmospheric pressure being admitted from Y and the resulting pressures on the mercury manometer D being measured. This volume was 112 c.c. It was necessary to keep the pressure in the bulb C fairly low, otherwise admitting a single volume of gas from X into the high vacuum side caused too great a change in the pressure as measured by the McLeod gauge.

The coconut charcoal used had been activated by the steam process, but before use it was reactivated by the "air oxidation" treatment. This was carried out by placing a shallow layer in a silica tube open at both ends and having an electric heating coil wound round it. The charcoal was heated to 450° C. for half-an-hour and air blown over its surface from time to time. The final sample was 8–10 mesh, hard and glossy and of bulk density 0·69.

A known weight of freshly reactivated charcoal was then placed in the bulb A, and the latter sealed to the main apparatus. The charcoal was completely outgassed by heating to 450° C. for 6 hours with the pumps working

continuously to remove any liberated gases. The charcoal was tested for complete outgassing by allowing it to cool, the tap H being closed, and the system at a pressure less than 10^{-5} mm. The charcoal was then reheated to 450° C. for half-an-hour with H open, the pumps being shut off, and if no increase in pressure resulted it could be safely assumed that outgassing was complete. It was found extremely important to ensure that all of the gas had been eliminated, as the amounts of gas adsorbed at the low pressures used in the experiments were very small, and any residual gas produced inconsistent results.

The actual adsorption of the various gases was measured in the following manner. The bulb Z containing the gas to be used was sealed to M, and the whole of the apparatus exhausted to a pressure below 10^{-5} mm. Taps E and F were then closed, and gas from Z admitted to C by alternately opening and closing the taps O and S. In this way the gas-pressure in C was raised to any convenient value.

Tap F was then opened so that a small volume of gas could be trapped between taps E and F. This volume was then admitted to the high vacuum side, tap H remaining closed during the operation. After 15 minutes the pressure of the gas was read on the gauge and noted. H was then opened and the gas admitted to the charcoal. When equilibrium conditions had been attained in the system the pressure was again noted, and from the initial and final pressures and the volume of the apparatus the amount of gas adsorbed by the charcoal was determined.

The tap H was again closed and the procedure described above repeated, the total quantity of gas adsorbed at the new equilibrium pressure being given by the summation of the previous amounts adsorbed while the pressure was changing from its initial to its final values. As the gases in the apparatus and in the charcoal are in equilibrium, it may be assumed that this sum is the amount of gas that would be adsorbed at the final pressure if the adsorption had occurred at one and the same time.

This process was repeated until the pressure-range 10^{-5} to 10^{-1} mm.—the limits of the gauge—had been covered. At the lower limit of this range one volume of gas admitted from EF caused a considerable change in the equilibrium pressure, but at 10^{-1} mm. about five amounts of gas from EF were necessary to cause an appreciable change in the equilibrium pressure as read on the McLeod gauge.

A correction was made for the volume of the charcoal bulb and the connecting tubing to H ; this correction was

negligible when relatively large adsorptions took place, as with oxygen, but finite with small adsorptions as in the case of nitrogen. The air temperature was read at one hour intervals and the average value noted.

Let V = volume in c.c. of the high vacuum side,

p_1 = original pressure in high vacuum side,

p_2 = final pressure.

Then the volume in c.c. of the gas, at 1 mm. pressure and room temperature, adsorbed by the charcoal is given by

$$V(p_1 - p_2).$$

The same sample of charcoal was used for carbon dioxide, nitrogen, and oxygen, but was replaced by a fresh quantity for carbon monoxide, owing to the fact that it was impossible to remove all the oxygen, previously adsorbed, from the charcoal. This second sample was treated in an exactly similar manner to the first. The quality of the first sample, as an adsorbent, improved after several "gassings" and "outgassings." This phenomenon is well known and has been investigated by Lemon *. It is one of the chief difficulties encountered when activated charcoal is used as a medium for the investigation of adsorption processes. Other substances, such as glass, wool, or mica, show varying adsorptive powers according to their previous treatment, but in no case is the discrepancy between the results of various experimenters more marked than with charcoal.

3. Experimental Results.

a. *Carbon Dioxide.*

The gas was prepared by the action of pure hydrochloric acid on freshly-boiled air-free marble in a Wolff bottle, and after passing over calcium chloride and phosphorus pentoxide, to remove the excess of water-vapour, it entered a small bulb Z with taps on the inlet and outlet tubes. A rapid stream of carbon dioxide was passed through the bulb for 2 hours, before closing the taps, to ensure the complete removal of atmospheric gases. The reservoir C was then charged from this bulb as described previously, the pressure of the gas in C being about 60 mm.

* Phys. Rev. vol. xiv. p. 282 (1919).

It was noted that at the low pressures employed carbon dioxide required a considerable time to attain equilibrium; comparatively rapid adsorption took place for the first 30 minutes, but was followed by slow adsorption during the succeeding 24 hours, and in some experiments continued for 3 days. Most of the gas was adsorbed during the first stage, and the slow adsorption that followed did not materially affect the volume adsorbed, but the final pressure attained depended on the time during which the gas was in contact with the charcoal. This time-effect was not observed below $0{\cdot}75 \times 10^{-3}$ mm. The effect has been studied, and the results obtained will be described in another paper.

During outgassing the last traces of carbon dioxide were removed with difficulty, and it was necessary to maintain the charcoal at 450° C. for 18 hours, the pumps maintaining the pressure below 10^{-4} mm. before it was entirely eliminated.

The results obtained with carbon dioxide are shown in Table I., the volumes absorbed per gram of charcoal being given in c.c. measured at 1 mm. and 15° C. During the whole of the experiments on carbon dioxide the temperatures never varied more than $\pm$ 1° C. from 15° C. In the third column, values of $\log_{10} \frac{\alpha}{P}$ are given, where α is the volume adsorbed per gram quoted at N.T.P., and P is the pressure in cm. of mercury.

TABLE I.

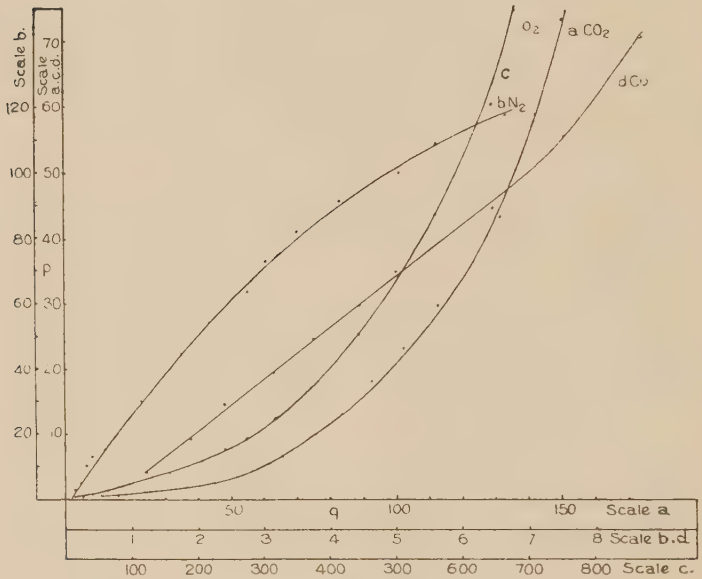
Adsorption of Carbon Dioxide at 15° C.

p.	q.	$\log_{10} \frac{\alpha}{P}$.
$0{\cdot}326 \times 10^{-3}$ mm.	5·165	2·2958
0·508	10·54	2·4129
0·729	15·44	2·4219
1·164	25·21	2·4309
2·515	45·17	2·3504
4·250	56·10	2·2166
6·378	65·63	2·1085
9·989	75·48	1·9743
17·85	92·70	1·8115
29·37	112·5	1·6791
42·78	131·2	1·5828
58·47	141·8	1·4808
73·02	150·5	1·4101

The graphical relation between p and q is shown in fig. 2, curve (a). At very low pressures, *i. e.* below $1{\cdot}5\times10^{-3}$ mm., the relation is linear and may be represented by

$$q=kp.$$

Fig. 2.



The results below 3×10^{-3} mm. are given on a larger scale in fig. 3, curve (a). The curve does not pass through the origin, but cuts the p axis at $1{\cdot}5\times10^{-4}$ mm. The continuity of the curve from the lowest to the highest pressures used indicates the absence of chemical action during adsorption, and is characteristic of a continuous series of solid solutions.

The adsorption equation

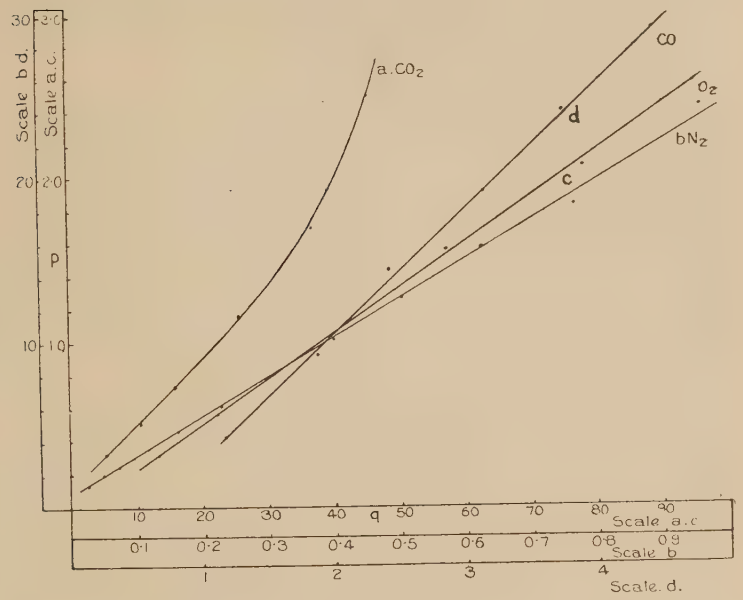
$$\alpha=kP^{\frac{1}{n}},$$

may be written in the form

$$\log\alpha=\log k+\frac{1}{n}\log P,$$

and fig. 4, curve (a), shows the relation between $\log_{10}\alpha$ and $\log_{10}P$. At first the curve is continuous, and its slope, *i.e.* the value of n, gradually increases. Above $2{\cdot}5\times10^{-3}$ mm. there is a linear relation between these quantities, n being constant and equal to $\frac{1}{0{\cdot}358}$.

Fig. 3.


Scale b d.
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Scale a.c
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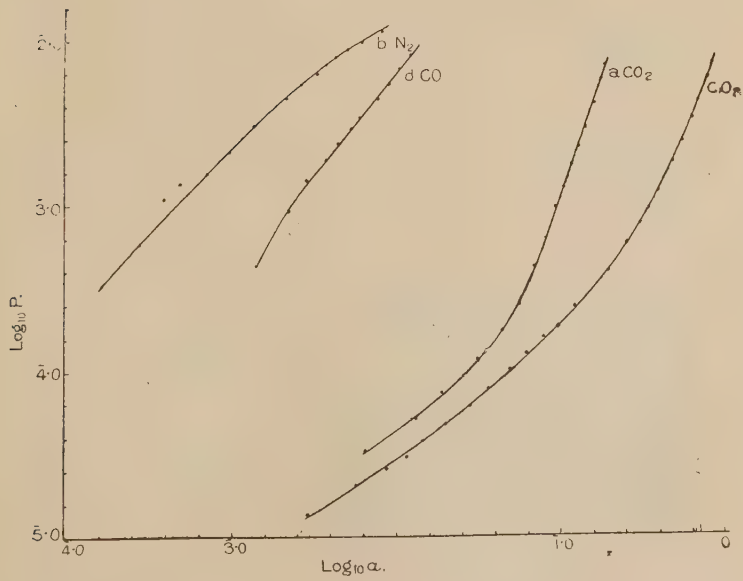
Scale. d.

Fig. 4.


b N2
d CO
a CO2
c O2
3·0
4·0
5·0
Log10 P.
4·0
3·0
1·0
0
Log10 a.

The values of $\frac{1}{n}$ have been determined for various pressures and are shown in Table II.

TABLE II.

Values of $\frac{1}{n}$ for carbon dioxide in the equation $\alpha = kP^{\frac{1}{n}}$.

Mean Pressure.	$0{\cdot}417\times10^{-3}$ mm.	$0{\cdot}836\times10^{-3}$ mm.	$1{\cdot}455\times10^{-3}$ mm.	$2{\cdot}130\times10^{-3}$ mm.
$\frac{1}{n}$	1·61	1·05	0·911	0·591

This decrease of $\frac{1}{n}$ with increase in equilibrium pressure is in agreement with the conclusions of Claude* and Titoff †, who found that $\frac{1}{n}$ decreased rapidly with increasing pressure.

Considering the relation between α and P proposed by Williams ‡ and Henry §, and plotting $\log_{10}\frac{\alpha}{P}$ against α ‖ in fig. 5, curve (a), it is found that there is a linear relation between these quantities only at pressures above $1{\cdot}75\times10^{-3}$ mm. As the pressure increases from the lowest values $\log\frac{\alpha}{P}$ increases with α, then becomes constant, and finally decreases uniformly. The values of A_0 and A_1 in the equation

$$\log\frac{\alpha}{P} = A_0 - A_1\alpha,$$

as determined from the graph, are

$$A_0 = 2{\cdot}788\ ;\ A_1 = 8{\cdot}578.$$

These results show that below $1{\cdot}5\times10^{-3}$ mm. there is a

* *Comp. Rend.* vol. clviii. p. 861 (1914).
Zeits. Phys. Chem. vol. lxxiv. p. 641 (1910).
‡ Proc. Roy. Soc. (Lond.) A, vol. xcvi. p. 287 (1919).
§ Phil. Mag. vol. xliv. p. 689 (1922).

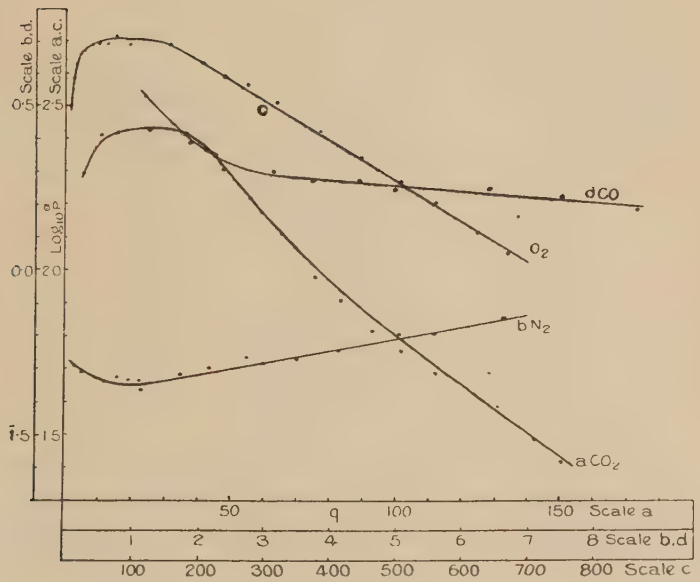
‖ More convenient to plot $\log_{10}\frac{\alpha}{P}$ and q.

linear relation between P and α, and above this pressure the relationship may be represented by either

$$\alpha = kP^{\frac{1}{n}}$$

or $$\log_{10}\frac{\alpha}{P} = A_0 - A_1\alpha.$$

Fig. 5.



b. *Nitrogen.*

The nitrogen used in these experiments was prepared by a method suggested by Waran *. When dilute ammonia is acted on by bromine water, the resulting nitrogen is free from all impurities except water-vapour.

The amount of this gas adsorbed was very small compared with that of carbon dioxide. The adsorption appeared to be instantaneous, and no time-effect could be detected ; in one particular experiment the charcoal remained in contact with the gas for three days, and no diminution in pressure during that period of time could be detected.

The outgassing of the charcoal after nitrogen had been used was comparatively rapid ; 6 hours' heating at 450° C. removed all the nitrogen that had been absorbed.

* Phil. Mag. vol. xlii. p. 246 (1921).

The results obtained are given in Table III.

TABLE III.

Adsorption of Nitrogen at 15° C.

p.	q.	$\log_{10}\frac{\alpha}{p}$.
$3{\cdot}231\times10^{-3}$ mm.	0·1313	$\bar{1}{\cdot}7050$
5·727	0·2212	$\bar{1}{\cdot}6829$
10·88	0·3145	$\bar{1}{\cdot}5570$
13·40	0·3810	1·5498
15·69	0·5705	$\bar{1}{\cdot}6567$
20·76	0·7782	$\bar{1}{\cdot}6698$
25·69	0·9521	$\bar{1}{\cdot}6645$
30·57	1·120	$\bar{1}{\cdot}6599$
45·10	1·734	$\bar{1}{\cdot}6808$
63·56	2·742	$\bar{1}{\cdot}7309$
82·33	3·503	$\bar{1}{\cdot}7249$
99·64	5·066	$\bar{1}{\cdot}8022$
108·8	5·588	$\bar{1}{\cdot}8066$
117·0	6·642	$\bar{1}{\cdot}8494$

The relation between p and q is shown in fig. 2 (*b*). The curve is different from the others obtained, in that it is convex towards the p axis. At pressures below 30×10^{-3} mm. there is a linear relationship, and this part of the curve has been enlarged in fig. 3 (*b*). As in the case with the carbon dioxide adsorption isotherm, the curve is continuous from the lowest to the highest pressures.

The quantities $\log_{10}\alpha$ and $\log_{10}P$ are plotted in fig. 4 (*b*), and the resulting curve is similar to the adsorption isotherm of nitrogen in that it is convex towards the $\log_{10}P$ axis. The curve below 40×10^{-3} is practically a straight line. The values of $\frac{1}{n}$ have been determined for various mean pressures, and are given in Table IV.

These values increase with rise in pressure, which result differs from that obtained by Claude and Titoff, and is also the reverse of that given by carbon dioxide.

The result of plotting $\log_{10}\frac{\alpha}{p}$ and q is given in fig. 5 (*b*). Below 30×10^{-3} mm. the curve is convex to the q axis, but above this pressure there is a linear relation between the

TABLE IV.

Values of $\frac{1}{n}$ for Nitrogen in the equation $x = kP^{\frac{1}{n}}$.

Mean Pressure.	4·479 $\times 10^{-3}$ mm.	10·72 $\times 10^{-3}$.	23·13 $\times 10^{-3}$.	42·52 $\times 10^{-3}$.	63·80 $\times 10^{-3}$.	82·22 $\times 10^{-3}$.	104·1 $\times 10^{-3}$.
$\frac{1}{n}$ ...	0·910	0·940	1·02	1·14	1·12	1·41	1·60

two quantities. It is, in fact, the reverse of that obtained with carbon dioxide. The values of A_0 and A_1 in the equation

$$\log_{10} \frac{c}{P} = A_0 - A_1 x.$$

are $A_0 = 0{\cdot}32$; $A_1 = 27{\cdot}4$.

c. *Oxygen.*

Oxygen was prepared by the action of acidulated potassium permanganate solution on hydrogen peroxide. These liquids were placed in Waran's * apparatus and the gas stored over phosphorus pentoxide before use.

It is well known that oxygen attains equilibrium, when in contact with charcoal at high pressures, only after the lapse of long periods of time, and this was found to be the case at the very low pressures used in these experiments. Within the range 10^{-5} to 10^{-3} mm. the rate of absorption was rapid, and equilibrium was practically reached within 30 minutes. Above 10^{-3} mm. the time required increased as the pressure was raised, and, at the highest pressures used, definite equilibrium was not attained after 5 days.

As stated previously, it was found impossible to remove all of the adsorbed oxygen by outgassing. This retentivity effect has been investigated by Lowry and Hulett †, who found that one-half of the adsorbed oxygen could be recovered at the ordinary outgassing temperature, but it was necessary to heat the charcoal to 1000° C. to recover the remaining gas, and this remainder was then emitted as carbon monoxide and carbon dioxide.

It was expected that as the boiling-point of carbon dioxide is higher than that of oxygen the amount of the latter gas

* *Loc. cit.*

† Jour. Amer. Chem. Soc. vol. xlii. p. 1401 (1920).

adsorbed would be less than that of the carbon dioxide, but in actual practice the quantities adsorbed were much greater. This may have been due to one or two reasons or a combination of both; either the previous gassings and outgassings had improved the adsorptive capacity of the charcoal, or a chemical compound may have been formed. Lowry and Hulett suggest that the adsorption of oxygen is accompanied by the formation of a carbon-oxygen complex, a stable solid oxide of carbon, at the surface of the charcoal at ordinary temperatures, but decomposed by heating to 1000° C. it dissociates into carbon monoxide and carbon dioxide. This second reason also accounts for the inability to remove all the adsorbed gas at 450° C.

In the results shown in Table V. it was assumed that equilibrium had been attained, at the higher pressures, after five days had elapsed. The amount adsorbed after this period, though measurable, was small compared with the total amount that had disappeared previously. The temperature throughout the investigation was slightly higher than for carbon dioxide, the mean value being 22° C.

Table V.

Adsorption of Oxygen at 22° C.

p	q.	$\log_{10}\frac{a}{p}$.
$0{\cdot}136\times10^{-3}$ mm.	2·299	2·3240
0·200	4·647	2·4622
0·253	6·955	2·5352
0·298	9·204	2·5858
0·375	11·47	2·5816
0·464	15·88	2·6304
0·608	22·48	2·6638
0·770	28·95	2·6712
1·011	39·50	2·6879
1·271	49·87	2·6897
1·582	62·19	2·6891
1·830	76·35	2·7163
2·452	95·85	2·6380
5·921	203·2	2·6315
9·277	274·2	2·5667
18·04	385·3	2·4256
33·95	506·2	2·2696
60·19	624·5	2·1120
74·49	670·1	2·0501

The adsorption isotherm for oxygen shown in fig. 2 (*c*) is similar in all respects to tbat obtained with carbon dioxide. At pressures below $2{\cdot}5 \times 10^{-3}$ mm. a linear relation holds, but above this pressure the curve is concave to the pressure-axis. The lower range of readings is shown in fig. 3 (*c*), and, as with the carbon-dioxide isotherm, the curve does not pass through the origin, but meets the pressure-axis at 8×10^{-5} mm. It is assumed that below this pressure the quantity adsorbed cannot be measured by the present apparatus.

The relation between $\log_{10}\alpha$ and $\log_{10}P$—fig. 3 (*c*)—resembles that for carbon dioxide, but at no pressure is a linear relationship evident. The values of $\frac{1}{n}$ calculated from this curve are given in Table VI., and, as is to be expected from the shape of the curve, $\frac{1}{n}$ decreases with increase in pressure. At the lower pressures this rate of decrease is rapid, but at higher pressures it becomes less, from which it is inferred that $\frac{1}{n}$ approaches a constant value.

TABLE VI.

Values of $\frac{1}{n}$ for Oxygen in the equation $\alpha = kP^{\frac{1}{n}}$.

Mean Pressure.	0·168 $\times 10^{-3}$ mm.	0·287 $\times 10^{-3}$.	0·494 $\times 10^{-3}$.	1·219 $\times 10^{-3}$.	2·895 $\times 10^{-3}$.	6·618 $\times 10^{-3}$.	13·67 $\times 10^{-3}$.	26·00 $\times 10^{-3}$.	47·07 $\times 10^{-3}$.
$\frac{1}{n}$ ...	1·82	1·44	1·39	1·11	0·915	0·673	0·512	0·432	0·366

Plotting values of $\log_{10}\frac{\alpha}{P}$ and q, the curve given in fig. 5 (*c*) is obtained. Concave to the q axis at low pressures it becomes a straight line at higher pressures. The values of the constants for this portion are $A_0 = 2{\cdot}88$; $A_1 = 0{\cdot}922$.

The results for oxygen below $2{\cdot}5 \times 10^{-3}$ mm. are best represented by a linear relation between P and α, but above 4×10^{-3} mm. the equation

$$\log_{10}\frac{\alpha}{P} = A_0 - A_1\alpha$$

gives an approximately true relation between α and P.

d. *Carbon Monoxide.*

Carbon monoxide was prepared by heating pure oxalic acid and concentrated sulphuric acid in a flask. The evolved gases were first passed through a wash-bottle and scrubbing chamber containing concentrated caustic potash solution, which removed carbon dioxide from the mixture. The resultant carbon monoxide then passed through phosphorus pentoxide and was stored in a bulb.

A new sample of charcoal was taken for this gas, as it was found that the old sample could not be effectively cleaned of the oxygen retained.

The amount of gas adsorbed was greater than with nitrogen, but less than with carbon dioxide. The adsorption was rapid and equilibrium was attained in 30 minutes ; at the higher pressures no time-effect could be detected. Outgassing was complete at 450° C. at the end of 10 hours.

The results obtained with this gas are shown in Table VII.

Table VII.

Adsorption of Carbon Monoxide at 20° C.

p.	q.	$\log_{10}\frac{\alpha}{P}$.
$4{\cdot}267\times10^{-3}$ mm.	1·181	0·5308
9·279	1·874	0·3936
14·42	2·417	0·3129
19·21	3·152	0·3036
24·27	3·730	0·2752
29·23	4·445	0·2706
34·66	4·986	0·2464
44·26	6·463	0·2529
55·08	7·551	0·2255
69·88	8·694	0·1833
85·56	10·31	0·1798

The adsorption isotherm is shown in fig. 2 (*d*), and is intermediate in shape to those for nitrogen and carbon dioxide. It is straight up to 40×10^{-3} mm., becoming slightly concave to the p axis above this pressure. That part of the curve below 30×10^{-3} mm. is shown on a larger scale in fig. 3 (*d*).

The result obtained by plotting $\log_{10}\alpha$ and $\log_{10}P$—fig. 4 (*d*)—is similar to the corresponding curve for nitrogen ; the concavity is towards the $\log_{10}\alpha$ axis, but becomes zero

above 12×10^{-3} mm. The value of $\frac{1}{n}$ for the latter part, *i. e.* from 12×10^{-3} mm. to 85×10^{-3} mm., is 0·826 ; below 12×10^{-3} mm. the mean value of $\frac{1}{n}$ is 0·600 at a mean pressure of $6{\cdot}6\times10^{-3}$ mm.

The $\log_{10}\frac{\alpha}{P}$, q curve—fig. 5 (*d*)—resembles the corresponding nitrogen curve, but the slope of the straight portion is in the same direction as that of the curves for oxygen and carbon dioxide. The values of the constants for this portion are $A_0=0{\cdot}316$: $A_1=6{\cdot}666$.

4. Discussion.

In considering the curves obtained for the various gases, it is advantageous to place the gases in the order of increasing boiling-points, *i. e.* nitrogen, carbon monoxide, oxygen, and carbon dioxide. The order of changes in the shape of the adsorption isotherm follows the same sequence. The nitrogen isotherm is a straight line for a considerable portion of its length, and then becomes slightly convex to the pressure-axis ; the carbon-monoxide isotherm is straight for about the same range of pressure as nitrogen, and then slightly concave to the pressure-axis ; the oxygen isotherm is straight for the same range of pressure and then decidedly concave to the pressure-axis ; the carbon-dioxide isotherm is straight for only a small range of pressure, and its concavity to the pressure-axis above this range is of the same order as that of the oxygen isotherm.

The change in shape in the $\log_{10}P$, $\log_{10}\alpha$ curves is also in the same sequence. That for nitrogen is slightly convex to the $\log_{10}P$ axis for the whole range covered ; the carbon-monoxide curve is slightly convex for a short portion, becoming a straight line for the higher pressures ; the oxygen curve is concave to this axis for the whole range ; the carbon-dioxide curve is concave for a short portion, after which it is straight.

A similar change is noted in the $\log_{10}\frac{\alpha}{P}$, q curves, the nitrogen curve being convex to the q axis for a small range, and then changing into a straight line sloping away from the q axis ; the carbon-monoxide curve is also convex for the same range as nitrogen, becoming a straight line with a

slope towards the q axis; the oxygen and carbon-dioxide curves are both concave to the q axis, becoming straight lines whose slopes to the q axis are greater than the corresponding slope of the carbon-monoxide curve.

The order of the quantities of gas adsorbed, neglecting the anomalous case of oxygen, is also in the same sequence.

At pressures below a critical pressure which varies for the various gases, the adsorption isotherm is best represented by the type of equation

$$\alpha = kP\ ;$$

i.e. $$\frac{1}{n} = 1.$$

This critical pressure is comparatively high for the gases of low boiling-point, being about 35×10^{-3} mm. for carbon monoxide and nitrogen; but with those gases of higher boiling-point and which are more easily adsorbed the critical pressure is considerably lower, being $2{\cdot}5 \times 10^{-3}$ mm. for oxygen and $1{\cdot}5 \times 10^{-3}$ for carbon dioxide. Hence it appears that the higher the boiling-point of the gas the lower is the critical pressure below which it can be assumed that the adsorption isotherm is a straight line.

The fact that $\frac{1}{n}$ does not equal unity at pressures below the critical pressure mentioned above suggests that

$$\alpha = kP^{\frac{1}{n}}$$

is not valid throughout a large pressure-range, although any curve of this type will be approximately a straight line for small values of α and P, *i.e.* near the origin; but from theoretical considerations it can be shown that the slope of this curve does not even approximate to the slopes obtained experimentally.

Transforming this equation to the form

$$P = \left(\frac{\alpha}{k}\right)^n,$$

we have $$\frac{dP}{d\alpha} = \frac{n\alpha^{n-1}}{k^n}.$$

Therefore at $\alpha = 0$, $\frac{dP}{d\alpha} = 0$ and the curve is tangential

to the α axis at the origin. So that

$$\alpha = kP^{\frac{1}{n}}$$

cannot be accepted as representing the relation between α and P at the pressures used in these experiments.

A consideration of the second type of adsorption equation suggested gives entirely different results:

$$\log_{10}\frac{\alpha}{P} = A_0 - A_1\alpha.$$

Then

$$\frac{\alpha}{P} = \epsilon^{2\cdot303(A_0 - A_1\alpha)},$$

$$\frac{dP}{d\alpha} = \epsilon^{-2\cdot303(A_0 - A_1\alpha)} + 2\cdot303\, A_1\alpha\, \epsilon^{-2\cdot303(A_0 - A_1)}.$$

At $\alpha = 0$,

$$\frac{dP}{d\alpha} = \epsilon^{-2\cdot303 A_0},$$

and the curve has therefore a definite slope at the origin.

Considering the values of $\frac{dP}{d\alpha}$ obtained by calculation from the above equation and also from the graphs in fig. 3, we have:

for Nitrogen $\frac{dP}{d\alpha} = 4\cdot055$,

the experimental value is 2·433;

for Carbon Monoxide $\frac{dP}{d\alpha} = 0\cdot479$,

the experimental value is 0·618;

for Oxygen $\frac{dP}{d\alpha} = 0\cdot00132$,

the experimental value is 0·00437;

for Carbon Dioxide $\frac{dP}{d\alpha} = 0\cdot00163$,

and the experimental value is 0·00335.

Although the calculated and experimental values of $\frac{dP}{d\alpha}$

do not agree absolutely, yet a comparison of their orders of magnitude suggests that

$$\log_{10}\frac{\alpha}{P} = A_0 - A_1\alpha$$

represents more accurately the adsorption isotherm than the usually recognized form

$$\alpha = kP^{\frac{1}{n}}.$$

The variation in the calculated and experimental results is due probably to the fact that it was necessary to calculate the values of A_0 from the more advanced portions of the curve.

At very low pressures, and correspondingly low values of α, the term $A_1\alpha$ is very small compared with the value of A_0, and at this stage

$$\log_{10}\frac{\alpha}{P} = A_0 = \text{constant};$$

i. e. there is a linear relation between α and P at very low pressures. This fact has been noted previously.

That $\log_{10}\frac{\alpha}{P}$ is a constant for a short range is illustrated in the curves for carbon dioxide and oxygen shown in fig. 5 ; with these gases the pressure-range over which this condition holds is from $0{\cdot}5\times10^{-3}$ to $1{\cdot}75\times10^{-3}$ mm. for carbon dioxide, and from $0{\cdot}5\times10^{-3}$ to $4{\cdot}0\times10^{-3}$ mm. for oxygen. The value of A_0 as given by the horizontal portion of the graph is slightly less than that obtained by calculation from the straight portion, being 2·43 for carbon dioxide and 2·72 for oxygen. Similar results do not occur on the curves for nitrogen and carbon monoxide. This is due probably to the fact that measurements of adsorption were not made below 4×10^{-3} mm. for these gases.

At pressures below $0{\cdot}5\times10^{-3}$ mm. the results obtained do not agree with the formula. The sudden decrease in the value of $\log_{10}\frac{\alpha}{P}$ must be accompanied by a change in the value of A_0, and to account for this change is very difficult. If the original assumptions from which Henry * deduced

* Phil. Mag. vol. xliv. p. 689 (1922).

the formula are examined, it is found that among other constants A_0 includes an expression for the field of molecular force, and the internal heat of evaporation of the molecules from the surface. A_0 is inversely proportional to the field of molecular force, and the heat of evaporation λ affects a term $\epsilon^{\frac{\lambda}{RT}}$, where ϵ, R, T have their usual significance. Therefore for A_0 to decrease, it must be assumed that there is either a sudden change in the field of molecular force which causes it to increase with decreasing pressure, or that the internal heat of evaporation decreases. Further investigation seems desirable.

5. Summary.

1. A method for determining the quantities adsorbed by activated charcoal at very low pressures is described.

2. Results have been obtained for nitrogen, carbon monoxide, oxygen, and carbon dioxide at air temperatures.

3. From a consideration of the adsorption isotherm of these gases, it is shown that the adsorption isotherm is better represented by

$$\log_{10}\frac{\alpha}{P} = A_0 - A_1\alpha$$

than by the more usual equation

$$\alpha = kP^{\frac{1}{n}}.$$

4. At very low pressures the value of $A_1\alpha$ is negligible compared with that of A_0, and the relationship between α and P is linear. The pressure at which this relationship no longer holds varies with the boiling-point of the gas ; it decreases as the boiling-point increases.

In conclusion, the Author wishes to express his sincere thanks to Prof. F. H. Newman for suggesting this branch of research, and for the keen interest he has taken and the helpful suggestions made throughout.

IX. *Fraunhofer Diffraction Phenomena for a General Polygonal Aperture.* *By* Enos E. Witmer, *Ph.D., Harrison Research Fellow, University of Pennsylvania* *.

[Plate III.]

ALTHOUGH the Fraunhofer diffraction patterns for apertures of various simple geometrical shapes have been studied in the classical researches on diffraction, it does not seem to be generally known that the principal features of the pattern can in all cases be described in very simple terms. The principal pattern is a radiate pattern, the centre of which is the image of the luminous point. Corresponding to each side of the aperture there are two rays, 180° apart, each perpendicular to the side in question. On the patterns obtained with small apertures these rays do not stand out so prominently, which is undoubtedly the reason why they are not emphasized in the theory of diffraction, but as the size of the aperture increases the minor features of the pattern fade into insignificance, leaving only the radiate figure. These rays appear, for example, on night photographs taken with cameras having an iris diaphragm which produces a polygonal aperture; each light source of sufficiently small angular diameter appears on such a picture as the centre of a number of divergent rays.

Historically it may be of interest to note that Sir John Herschel † observed these ray patterns in his telescope. Lloyd ‡ and J. W. Gordon § also refer to them, while Airy ‖ worked out the mathematical theory for the case of the equilateral triangle, and showed that the principal pattern consists of six rays. Schwerd ¶ derived mathematically the patterns for various simple geometrical apertures.

No one, however, seems to have demonstrated mathematically that, in the case of the general polygonal aperture, the principal pattern conforms to the description given above. This demonstration is made below. The theory shows, furthermore, that in certain cases these rays have a fringe structure, while in other cases they do not. This result seems to be new, and has subsequently been confirmed experimentally.

* Communicated by Prof. C. B. Bazzoni.

† Sir John Herschel, 'Encyclopedia Metropolitana,' "Light," Art. 772.

‡ Lloyd, 'The Wave Theory of Light,' pp. 126–127.

§ J. W. Gordon, Proc. Phys. Soc. Lond. xxiv. pp. 422–448 (1912).

‖ Airy, 'Mathematical Tracts,' pp. 316–318.

¶ Schwerd, *Die Beugungserscheinungen.*

The aperture is assumed to be plane. Using rectangular Cartesian coordinates, we shall take the plane of the aperture as the xy-plane, and the origin in or very near the aperture. Let (u_1, v_1, w_1) be the coordinates of the centre of the luminous disturbance incident on the aperture, and (u_0, v_0, w_0) the point in or very near the focal plane at which the effect is to be determined.

Let
$$\rho_1^2 = u_1^2 + v_1^2 + w_1^2,$$
$$\rho_0^2 = u_0^2 + v_0^2 + w_0^2.$$

Then the effect at the point (u_0, v_0, w_0) is given in terms of the wave-function by the well-known formula *

$$\phi_0(\tau) = -\frac{A}{\lambda}\frac{1}{\rho_1\rho_0}\frac{\partial\rho_0}{\partial z}e^{ik\omega\tau}\iint i\, e^{i(px+qy)}\,dx\,dy, \quad . \quad (1)$$

where the integration is over the surface of the aperture, and

$$\left.\begin{aligned} p &= \frac{2\pi}{\lambda}\frac{1}{\rho_0}(u_0-u_1) \equiv \frac{2\pi}{\lambda}\frac{r}{\rho_0}, \\ q &= \frac{2\pi}{\lambda}\frac{1}{\rho_0}(v_0-v_1) \equiv \frac{2\pi}{\lambda}\frac{s}{\rho_0}. \end{aligned}\right\} \quad . \quad . \quad (2)$$

A and ω are constants, $k = \dfrac{2\pi}{\lambda}$, λ is the wave-length of light, τ is time, and $i = \sqrt{-1}$.

Let
$$\left.\begin{aligned} r &= u_0 - u_1, \\ s &= v_0 - v_1. \\ t &= w_0 - w_1. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since in the case of Fraunhofer diffraction phenomena the centre (u_1, v_1, w_1) of the luminous disturbance incident on the aperture is the image of the radiant point, r. s, and t are the coordinates of the point considered on the screen of observation referred to the radiant point as origin. Hereafter, in referring to the point (u_0, v_0, w_0), we shall use the coordinates (r, s, t).

It is evident that we may rotate the x- and y-axes about the z-axis into any position we choose. We shall therefore choose these axes so as to make $s = q = 0$ for the particular point considered, thereby simplifying the integration in (1).

Now consider an aperture which has the shape of an

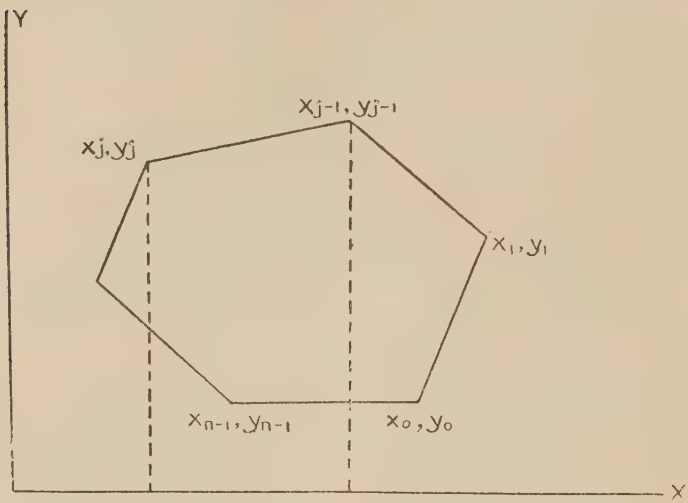
* *See* Walker, 'Analytical Theory of Light' (Camb. Univ. Press, pp. 96–99.

irregular polygon of n sides. Let the xy-coordinates of the n vertices be

$$(x_0, y_0), (x_1, y_1), \ldots\ldots (x_{n-1}, y_{n-1}), (x_n, y_n) \equiv (x_0, y_0),$$

as indicated in fig. 1.

Fig. 1.



Let us call the side whose end-points are (x_{j-1}, y_{j-1}) and (x_j, y_j) the side j, and the quadrilateral whose vertices are

$$(x_{j-1}, y_{j-1}), (x_j, y), (x_j, 0), (x_{j-1}, 0),$$

as is indicated in fig. 1, the quadrilateral j.

The equation of side j is

$$\frac{y_{j-1}-y}{x_{j-1}-x} = \frac{y_j-y}{x_j-x} = \frac{y_j-y_{j-1}}{x_j-x_{j-1}} = m, \quad . \quad . \quad . \quad (4)$$

whence

$$y_j - m_j x_j = y_{j-1} - m_j x_{j-1}. \quad . \quad . \quad . \quad . \quad (4\,a)$$

Since $q=0$, the integral in (1) taken over the quadrilateral j is

$$\iint i e^{ipx} dx\, dy = \int_{x_j}^{x_{j-1}} i(y_j + m_j x - m_j x_j) e^{ipx}\, dx.$$

Using equation (4 a) we obtain

$$\iint i e^{ipx} dx\, dy = \frac{1}{p}(y_{j-1} e^{ipx_{j-1}} - y_j e^{ipx_j}) + \frac{i m_j}{p^2}(e^{ipx_{j-1}} - e^{ipx_j}). \quad (5)$$

The integral over the polygon is evidently given by the expression

$$J(r, 0, t) \equiv \iint_{\gamma} ie^{ipx} dx\, dy = \sum_{j=1}^{n} \int_{x_j}^{x_{j-1}} i(y_j + m_j x - m_j x_j) e^{ipx}\, dx$$

$$= \sum_{j=1}^{n} \frac{im_j}{p^2} (e^{ipx_{j-1}} - e^{ipx_j}). \quad . \quad . \quad (6)$$

This is the expression for the integral J if none of the m_j's are infinite. If the xy-axes have been so chosen as to make some of the slopes m_j infinite, we must evaluate the indeterminate terms in (6). Remembering that if $m_\sigma = \infty$, $x_\sigma = x_{\sigma-1}$, we get in this case

$$0, t) = \sum_j \frac{im}{p^2} (e^{ipx_{j-1}} - e^{ipxj}) + \sum_\sigma \frac{y_\sigma - y_{\sigma-1}}{p} e^{ipx\sigma}, \quad (7)$$

where the first summation is over the finite slopes m_j and the second over the infinite slopes. Since $x_\sigma = x_{\sigma-1}$, $y_\sigma - y_{\sigma-1} = \pm l_\sigma$, where l_σ is the length of the side σ.

The terms in $\frac{1}{p^2}$ in (6) and (7) will be negligible in comparison with those in $\frac{1}{p}$, provided that in general

$$\frac{m_j}{p(y_\sigma - y_{\sigma-1})} \text{ is small.}$$

This will be so, if pL is sufficiently large, where L is the average length of a side of the polygonal aperture. Using equation (2), this condition reduces to the condition that $\frac{1}{\lambda} \frac{L}{\rho_0} r$ be sufficiently large. Since the point under consideration is $(r, 0, t)$ for the particular plane of observation $t = 0$, which is parallel to the plane of the aperture, r is the radial distance of the point considered from the image of the luminous point. Since λ is always very small in the case of visible or ultra-violet light, this is not a stringent condition, but it does exclude a certain region about the image of the luminous point where r is too small. Under this condition (6) and (7) reduce respectively to

$$J(r, 0, t) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$J(r, 0, t) = \sum_\sigma \frac{y_\sigma - y_{\sigma-1}}{p} e^{ipx\sigma}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Let us consider the expression J in equation (9). Using equation (2), we see that $J(r, 0, t) = J(r)$—that is, J is

a function of r alone, all the other quantities being constants. It can be shown that $J(r)$ cannot be identically zero in any case, since no two of the x_σ's can be equal. Furthermore, $J(r)$ can vanish for only an enumerable infinity of values of r, so that the values of r at which $J(r) \neq 0$, regarded as a set of points, is *everywhere dense*. Since in any practical case the range of r is limited, it is easy to see that $J(r)$ will vanish for only a finite number of values of r in that range.

The intensity I is obtained by substituting $J(r, 0, t)$ for the integral in (1), and multiplying this result by its conjugate. Since $I(r, 0, t)$ vanishes when, and only when, $J(r, 0, t)$ vanishes, we see from (8) and (9) that $I=0$ at all the points $(r, 0, t)$ except when some of the slopes are infinite, in which case the intensity is finite at an everywhere dense set of points in the rt-plane in a certain region about the image of the luminous point. Now the fact that the slope of a side is infinite means that the y-axis is parallel to that side, and the rt-plane is perpendicular to the y-axis. Regarding the xy-axes as rotating about the z-axis, and therefore the rs-axes as rotating about the t-axis, it follows that all the points of finite intensity lie in planes through the image of the radiant point that are perpendicular to the sides of the aperture, and on these planes the points of finite intensity are everywhere dense in a certain region about the image of the luminous point. It is easily seen now that the pattern on any plane through the image of the radiant point is a radiate pattern whose centre is the image point, and that corresponding to each side of the aperture there are two bright rays, 180° apart, perpendicular to the side in question. We have therefore demonstrated the rule stated in the first paragraph.

Having demonstrated the existence of these rays, we shall next consider their structure. We shall limit our discussion to the pattern on the plane $t=0$, which is parallel to the plane of the aperture. In this case r is the radial distance of the point considered $(r, 0, 0)$ from the image of the radiant point. Since t does not appear in the formulas for I and J, the pattern on any other plane P through the image of the radiant point is obtained by projecting the pattern on the plane $t=0$ on to the plane P by a family of lines normal to the plane of aperture.

First consider the case when there is no other side parallel to the side in question, which we will assume to be the side 1. Then from (9) the corresponding value of J is

$$J(r, 0, t) = \frac{y_1 - y_0}{p} e^{ipx_1}, \quad . \quad . \quad . \quad . \quad (10)$$

and the intensity of the corresponding ray is

$$I(r, 0, t) = \left(\frac{A}{2\pi}\frac{1}{\rho_1}\frac{\partial \rho_0}{\partial z}\right)^2 \frac{l_1^2}{r^2}. \quad . \quad . \quad . \quad . \quad (11)$$

Equation (11) shows that in this case the rays do not have a fringe structure, but that the intensity falls off uniformly as the inverse square of the radial distance. Furthermore, the intensity is proportional to the square of the length of the corresponding side.

When two sides of the aperture, 1 and σ, are parallel, the corresponding value of J is

$$J(r, 0, t) = \frac{1}{p}\left[(y_1 - y_0)e^{ipx_1} + (y_\sigma - y_{\sigma-1})e^{ipx_\sigma}\right]$$

$$= \frac{e^{\frac{1}{2}ip(x_1+x_\sigma)}}{p}\left[(l_1 - l_\sigma)\cos ap + i(l_1 + l_\sigma)\sin ap\right], \quad (12)$$

where $2a = x_1 - x_\sigma =$ the distance between the parallel sides. Hence the intensity distribution * along the corresponding rays is

$$I(r, 0, t) = \left[\frac{A}{2\pi}\frac{1}{\rho_1}\frac{\partial \rho_0}{\partial z}\frac{1}{r}\right]^2\left[(l_1 - l_\sigma)^2\cos^2 ap + (l_1 + l_\sigma)^2\sin^2 ap\right]. \quad . \quad (13)$$

In this case the corresponding rays exhibit maxima and minima of intensity which are more or less pronounced according as l_1 and l_σ are or are not equal.

These two cases are the ones most commonly met with. It is only in the case of polygons with re-entrant angles that more than two sides can be parallel to each other, and the formulas for the intensity of the corresponding rays become complicated.

These conclusions as to the structure of the rays were verified experimentally. Photographs were taken with a large camera equipped with a telephoto lens. A carbon arc with a cap attachment for getting a point source was used as the source of light. The diffracting diaphragm, which was made of razor-blades fastened on cardboard, was set up in front of the lens. Fig. 2 (Pl. III.) shows the pattern obtained with a triangular aperture, the triangle being approximately equilateral. These rays do not show a fringe structure. This same diaphragm was taken and the triangle converted into a trapezoid by adding another blade in such a way as to cut off about half the altitude. The pattern

* Equation (13) applies to the case when $(y_1 - y_0)$ and $(y_\sigma - y_{\sigma-1})$ have opposite signs. If these two quantities have like signs, which can occur only in the case of a polygon with re-entrant angles, the quantities $(l_1 - l_\sigma)$ and $(l_1 + l_\sigma)$ must be interchanged in equation (13).

obtained with this diaphragm is shown in fig. 3 (Pl. III.). The vertical rays, which are due to the parallel sides of the aperture, have a fringe structure in accordance with theory. The other four rays are due to the remaining sides of the trapezoid, and show no fringes. The differences in the intensities of the vertical and non-vertical rays is due to the differences in the length of the sides producing the rays, as equations (11) and (13) show. The fringes in fig. 3 (Pl. III.) show much more distinctly on the original negative than in the reproduction, and the central part of the patterns in both figures is obscured by halation.

A number of figures, not published here, were also obtained with large diffracting apertures of various shapes, using an ordinary camera and a point source of light. In some cases the iris diaphragm of the camera, set at F 8 or F 11, was used as the diffracting aperture. In every case the patterns conform to the description given above, except that with the large apertures the fringe structure does not appear because the fringes are too fine-grained.

Summary.

The preceding analysis demonstrates, and experiment verifies, the following conclusions :—

(1) The most prominent features of the Fraunhofer diffraction pattern for a general polygonal aperture form a radiate figure, consisting of bright rays diverging from the image of the luminous point. Corresponding to each side of the aperture there are two rays, 180° apart, perpendicular to that side.

(2) These rays may, or may not, have a fringe structure. If there is no other side of the aperture parallel to the side in question, the two rays corresponding do not have a fringe structure, the intensity in each ray decreasing uniformly from the centre outward. If, however, one or more sides of the aperture are parallel to the side in question, the two rays corresponding exhibit maxima and minima of intensity.

These conclusions are based on an approximation which is not valid in a certain region about the centre of the figure, a region which is in many cases vanishingly small, but in other cases is very large.

In conclusion, the writer wishes to acknowledge his indebtedness to Dr. H. C. Richards for valuable suggestions regarding the experimental work.

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July 27, 1925.

X. *Langevin's Theory of Ionic Mobility.* *By* H. R. Hassé, *M.A., D Sc., Professor of Mathematics in the University of Bristol* *.

THE calculations given in this paper originated in the proposal to apply to the theory of ionic mobility the rigorous methods which have been introduced into the kinetic theory of gases by Chapman † and Enskog ‡. It is known from the work of these investigators that calculations based on the use of the "mean free path," whilst they give a general descriptive view of the phenomena, may lead to quite erroneous results, not only in regard to the numerical factors occurring in the equations, but also in regard to the dependence of the phenomena on the various physical quantities involved. The results obtained by Chapman and Enskog have cleared up many points of difficulty which had arisen, and brought about a harmony and a consistency which was lacking in the older treatments.

The need of a satisfactory theory of mobility was pointed out to me by my colleague Professor Tyndall, and I had completed some of the necessary calculations before discovering that the subject had been exhaustively treated by Langevin § in a paper which is of fundamental importance, and which seems to have been frequently neglected, and sometimes misunderstood, by writers on this subject.

Apart from its application to mobility Langevin's work is of great interest, as it provides the only case, up to the present time, in which a detailed treatment of the influence on elastic collisions of attractive forces of any magnitude has been given. Sutherland's well-known procedure, which has been treated rigorously by Enskog and James ‖, only deals with the effect of weak forces of attraction, and is therefore only a first approximation to the general case. For this reason, and also in view of future applications, it was considered worth while to make a recalculation of the numerical part of the paper, the results of which are given by Langevin in a curve from which they cannot be obtained with any great accuracy.

* Communicated by the Author.

† Chapman, Phil. Trans. A, ccxi. (1912), ccxvi. (1916), and ccxvii. (1918).

‡ Enskog, 'Kinetische Theorie der Vorgänge in mässig verdünnten Gasen' (1917).

§ Langevin, *Ann. de Chimie et de Physique*, (8) v. p. 245 (1905).

‖ Enskog, *loc. cit.*; James, Proc. Cam. Phil. Soc. xx. p. 447 (1921).

I. General Statement of the Theory.

1. *Langevin's Theory.*

The problem of the motion of the ions under the influence of an external field and the field of the molecules is a problem in the kinetic theory of diffusion. The ion is represented as a positive or negative charge of magnitude e, the charge on an electron, and the model chosen for the molecule is that of a perfectly conducting sphere. The attractive force between the ion and the molecule is then due to the induced charge on the latter, and is equal to

$$\frac{e^2a^3(2r^2-a^2)}{r^3(r^2-a^2)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the electrical radius of the molecule, and r the distance of the ion from the centre of the sphere *.

If r is assumed to be always large compared with a, this force is

$$2e^2a^3/r^5, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and if K is the dielectric constant of the gas containing N molecules per unit volume, we have

$$K-1=4\pi Na^3 \dagger. \quad . \quad . \quad . \quad . \quad (3)$$

whence the force of attraction is given by

$$(K-1)e^2/2\pi Nr^5. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The expression (4) for the attractive force is also the first term in a series which would give the force on any assumption as to the size and shape of the neutral molecules.

The rigorous mathematical treatment of problems in the kinetic theory is very complicated, and the results can only be obtained by a process of successive approximation. Fortunately, the first approximation is a very good one and, in the case of diffusion under consideration, this was obtained by Langevin in the paper referred to : (i.) when the molecules are perfectly elastic spheres, and (ii.) when in addition the molecules exert attractive forces of the type given by equation (4).

* *Cf.* J. J. Thomson, 'Elements of the Mathematical Theory of Electricity and Magnetism,' 5th edition, p. 114.

† *Cf.* Jeans, 'Mathematical Theory of Electricity and Magnetism,' p. 131 (1908).

Using, to a large extent, Langevin's notation, the mobility k is expressed in the form

$$k = \frac{A}{\sqrt{\rho(K-1)}}\left(1+\frac{m}{M}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (5)$$

where ρ is the density of the gas, M the mass of the ion, and m that of a molecule of the gas, whose concentration is large compared with that of the ions, and A is a numerical coefficient. The value of A has been calculated in the case of a *repulsive* centre of force varying inversely as the nth power of the distance for various values of n by Maxwell ($n=5$), and Chapman ($n=7$, 9, 11, 15, and ∞) *.

When the force is *attractive*, and collisions take place, the value of A will depend on the comparative effect of the attractive forces and the elastic collisions. Langevin introduces a symbol μ ($\equiv\lambda^{-1}$) given by

$$\mu^2 = \frac{(K-1)e^2}{8\pi p\sigma^4}, \quad \lambda^2 = \frac{8\pi p\sigma^4}{(K-1)e^2}, \quad . \quad . \quad . \quad (6)$$

where p is the pressure of the gas, and σ is the distance between the centres of the molecule and the ion at the instant of collision, and A is then calculated as a function of λ; it is this calculation of A in terms of λ which is an important feature of Langevin's paper.

When λ is small, either σ must be small or $(K-1)$ large, so that the attractive forces are of much greater importance than the collisions, and in this case A tends to a limiting value given by Langevin as 0·505.

Equation (5) may be written in the form

$$k = \lambda A\frac{e}{\sigma^2(8\pi p\rho)^{\frac{1}{2}}}\left(1+\frac{m}{M}\right)^{\frac{1}{2}}, \quad . \quad . \quad . \quad (7)$$

and in the case when λ is large, *i. e.* the attracting forces are weak, $\lambda A \longrightarrow 0{\cdot}75$, so that k tends to the value

$$\frac{3}{4}\frac{e}{\sigma^2(8\pi p\rho)^{\frac{1}{2}}}\left(1+\frac{m}{M}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Experiments on positive ions show that the mobility varies inversely as the pressure over a large range of pressure. For negative ions this law does not hold over as wide a range, which may be attributed to the presence at low pressures of free electrons in this case. If the temperature is kept constant, ρ will vary as p, and if we may assume that

* Chapman, Mem. and Proc. Man. Lit. and Phil. Soc. lxvi. p. 1 (1922).

$(K-1)$ varies also as p in accordance with the Clausius-Mosotti theory of dielectrics, then from (6) λ is independent of the pressure, and therefore from (5) and (7) the mobility should vary as p^{-1}. Thus these formulæ are in agreement with those given by other theories in predicting the same law of variation of mobility with pressure.

Before proceeding further, it is necessary to inquire how allowance can be made for the fact that equation (5) is only a first approximation to the correct formula. It has been shown by Chapman and Enskog that, in the case of elastic collisions, the equation for the diffusion of gases, and hence equation (5) which is derived from it, gives results which are about 13 per cent. too small, and that the equation is exact in the other extreme case, when we are dealing only with forces varying inversely as the fifth power of the distance. For intermediate cases where both collisions and attractive forces are operative, we may safely say that the correcting factor will lie between 1·00 and 1·13, but its value has not yet been determined, and it will be evident later on that its calculation would introduce a refinement which is not justified by the present state of either the theoretical or the experimental side of the subject. In the calculations of mobility in Section III. it has therefore been considered sufficient to take the value of the Chapman-Enskog correcting factor as unity, except when $\lambda \geq 2{\cdot}3$ (when the effect of the collisions predominates), in which case its value has been taken as 1·13.

2. *Comparison with other Theories.*

The important features of Langevin's theory can best be brought out by a discussion of certain other formulæ for the mobility which have been given, and which are based on the older type of kinetic theory.

Wellisch * gave an expression for k which, in the notation of this paper, is

$$k = \frac{e}{\pi\sigma^2}(3p\rho)^{-\frac{1}{2}}\left(\frac{m}{\mathrm{M}}\right)^{\frac{1}{2}}\left(1+\frac{\mathrm{M}}{m}\right)^{-\frac{1}{2}}\left(1+\frac{2}{3\lambda^2}\right)^{-1}, \quad (9)$$

which cannot be expected to apply to strong attractive forces since $k \longrightarrow 0$ as $\lambda \longrightarrow 0$. For weak attractive forces when λ is large, (9) becomes

$$k = \frac{e}{\pi\sigma^2}(3p\rho)^{-\frac{1}{2}}\left(\frac{m}{\mathrm{M}}\right)^{\frac{1}{2}}\left(1+\frac{\mathrm{M}}{m}\right)^{-\frac{1}{2}} \quad . \quad . \quad . \quad (10)$$

* Wellisch, Phil. Trans. A, ccix. p. 249 (1909).

Another example of a formula for the mobility of which use has been made in the discussion of experimental results is that given by J. J. Thomson* in the course of an interesting consideration of theories of ionic mobility, viz. :—

$$k=\frac{3}{4}\frac{e}{\pi\sigma^2}(3p\rho)^{-\frac{1}{2}}\frac{\left(1+\frac{m}{3\mathrm{M}}\right)}{\left(1+\frac{m}{5\mathrm{M}}\right)}\left(1+\frac{m}{\mathrm{M}}\right)^{\frac{1}{2}}, \quad . \quad . \quad (11)$$

where $m \leqslant \mathrm{M}$, the only case we need consider.

This formula is based on the "mean free path" method, corrected for the phenomenon of persistence of velocity, and assumes that the only interaction of a molecule and an ion is that of an elastic collision.

Equations (8), (10), and (11), which all apply to weak attractive forces, are directly comparable, and it is evident that they differ both in their numerical values and in their dependence on the ratio of m to M.

For the case of a mono-molecular ion when $\mathrm{M}=m$, the formulæ will give values for the mobility in the ratio

$$1 : \frac{4}{3}\left(\frac{2}{3\pi}\right)^{\frac{1}{2}} : \frac{20}{9}\left(\frac{2}{3\pi}\right)^{\frac{1}{2}},$$

or $$1 : 0{\cdot}614 : 1{\cdot}023.$$

This will account to a great extent for the fact that Wellisch's calculated values for such an ion are much smaller than those given in Section III. as determined from Langevin's formula.

As regards the dependence on the ratio m/M, we see that as this ratio increases from 0 to 1, the mobility, as calculated from the formulæ (8), (10), and (11), will increase in the ratios

$$1 \text{ to } \sqrt{2},\ 0 \text{ to } 1/\sqrt{2}, \text{ and } 1 \text{ to } 10\sqrt{2}/9,$$

respectively. Now it is known from experiment that the mobility of an ion depends only on the gas into which it is introduced. The simplest way of accounting for this important fact is to make the formulæ almost independent of the mass M of the ion, which in the case of (8) and (11) can be done by taking M to be large compared with m, i. e. by assuming that the ion is clustered with molecules of the gas. This is not possible on Wellisch's formula (10), which will give mobilities varying widely with changes in the value of the ratio m/M.

* J. J. Thomson, Proc. Phys. Soc. xxvii. p. 94 (1914–15).

J. J. Thomson has, in addition to the case of elastic collisions, considered also the other extreme case of strong attractive forces of the type (4), and gives the formula (5) without determining the numerical value of the constant A. Langevin's theory includes both these types of interaction of an ion and a molecule, and can thus be used when both are operative at the same time.

II. Calculation of A as a Function of λ.

The course of the calculation of A as a function of λ is mapped out in Langevin's paper, but it seems advisable to give it in greater detail in order to facilitate any checking that may be necessary in future.

The quantity A is given by 3/16Y, where

$$Y \equiv \int_0^\infty y e^{-z^2 z^4} dz, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and

$$y \equiv \int_0^\infty \cos^2\theta \, d(\beta^2). \quad . \quad . \quad . \quad . \quad (13)$$

In these expressions

$$z = V\left(\frac{hm\mathrm{M}}{m+\mathrm{M}}\right)^{\frac{1}{2}}$$

where V is the relative velocity of the ion and molecule before the encounter, $h^{-1} = 2k\mathrm{T}$, where k is the ordinary gas constant, $\pi - 2\theta$ is the angle through which the relative path is deflected by the encounter, and β^2 is a variable connected with θ by an equation obtained from the dynamics of the encounter, viz.:—

$$\theta = (2\beta^2)^{\frac{1}{2}} \int_0^{x_1} \frac{dx}{(1-2\beta^2 x^2 + x^4)^{\frac{1}{2}}}. \quad . \quad . \quad . \quad (14)$$

In (14) x_1 is the least root of the denominator, if it exists, and is less than $(\lambda z)^{-\frac{1}{2}}$, and x_1 is equal to $(\lambda z)^{-\frac{1}{2}}$ if this is not the case. There are therefore three cases to consider:

(i.) When $\beta > 1$, so that x_1 is given by

$$x_1^2 = \beta^2 - \sqrt{(\beta^4 - 1)}, \quad . \quad . \quad . \quad . \quad (15)$$

and x_1 so determined is less than $(\lambda z)^{-\frac{1}{2}}$. The relative orbit has then an apse at a distance from the centre of the ion greater than σ, so that no collision can occur.

(ii.) When $\beta > 1$, but $x_1 > (\lambda z)^{-\frac{1}{4}}$. In this case the apse is at a distance from the centre of the ion less than σ, so that an elastic collision does occur.

(iii.) When $\beta < 1$. In this case there is no apse, so that a collision is bound to take place, and then $x_1 = (\lambda z)^{-\frac{1}{4}}$.

The integral (14) can be reduced in all cases by trigonometrical substitution to forms which enable θ to be expressed in terms of elliptic functions :

(i.) Put $2\beta^2 = \sin\alpha + \operatorname{cosec}\alpha$, $x = (\sin\alpha)^{\frac{1}{2}}\sin\phi$, and then

$$\theta = \sqrt{(1+\sin^2\alpha)}\int_0^{\frac{\pi}{2}} \frac{d\phi}{(1-\sin^2\alpha\sin^2\phi)} = \sqrt{(1+\sin^2\alpha)}\,\mathrm{K}\left(\frac{\pi}{2},\alpha\right),$$

using the ordinary notation for elliptic integrals.

(ii.) With the same substitution for β^2 and x, the upper limit ϕ_1 of the integral is given by

$$\sin\phi_1(\sin\alpha)^{\frac{1}{2}} = (\lambda z)^{-\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (16)$$

so that

$$\theta = \sqrt{(1+\sin^2\alpha)}\,\mathrm{K}(\phi_1,\alpha).$$

(iii.) The substitutions $\beta^2 = \cos 2\gamma$, $x = \tan\frac{1}{2}\phi$, reduce the integral (14) to

$$\theta = \frac{1}{2}\int_0^{\phi_1} \frac{d\phi}{(1-\cos^2\gamma\sin^2\phi)^{\frac{1}{2}}} = \frac{1}{2}\mathrm{K}(\phi_1,\tfrac{\pi}{2}-\gamma)$$

where $(\lambda z)^{-\frac{1}{2}} = \tan\frac{1}{2}\phi_1$ and $\lambda z > 1$.

When $\lambda z < 1$, we write $x = \cot\frac{1}{2}\phi$, and then

$$2\theta = 2\int_0^{\frac{\pi}{2}} \frac{d\phi}{(1-\cos^2\gamma\sin^2\phi)^{\frac{1}{2}}} - \int_0^{\phi_2} \frac{d\phi}{(1-\cos^2\gamma\sin^2\phi)^{\frac{1}{2}}}$$

$$= 2\mathrm{K}\left(\frac{\pi}{2},\frac{\pi}{2}-\gamma\right) - \mathrm{K}\left(\phi_2,\frac{\pi}{2}-\gamma\right)$$

and ϕ_2 is given by $(\lambda z)^{-\frac{1}{2}} = \cot\frac{1}{2}\phi_2$.

The calculation of θ from (14) has now to be considered om the point of view of the values of λz. We then have e following table which, except for slight changes in

notation and the correction of two misprints, is copied from Langevin's paper :—

First Type. $z\lambda \equiv \operatorname{cosec}\epsilon > 1$.

$$\beta < 1,\ 2\theta = \sqrt{(2\cos 2\gamma)}\,\mathrm{K}\left(\phi_1, \frac{\pi}{2} - \gamma\right).$$

$$\beta^2 \equiv \tfrac{1}{2}(\sin\alpha + \operatorname{cosec}\alpha) > 1 \begin{cases} 0 < \alpha < \epsilon, \\ \qquad \theta = \sqrt{(1+\sin^2\alpha)}\,\mathrm{K}\left(\frac{\pi}{2}, \alpha\right). \\ \epsilon < \alpha < \frac{\pi}{2}, \\ \qquad \theta = \sqrt{(1+\sin^2\alpha)}\,\mathrm{K}(\phi_1, \alpha). \end{cases}$$

Second Type. $z\lambda < 1$.

$$\beta < 1,\ 2\theta = \sqrt{(2\cos 2\gamma)}\left[2\mathrm{K}\left(\frac{\pi}{2}, \frac{\pi}{2} - \gamma\right) - \mathrm{K}\left(\phi_2, \frac{\pi}{2} - \gamma\right)\right].$$

$$\beta^2 = \tfrac{1}{2}(\sin\alpha + \operatorname{cosec}\alpha) > 1,\ \theta = \sqrt{(1+\sin^2\alpha)}\,\mathrm{K}\left(\frac{\pi}{2}, \alpha\right).$$

The calculation of y from (13) for the second type ($z\lambda < 1$) is fairly straightforward, both for $\beta > 1$ and < 1. The values of the elliptic integrals were taken from Legendre's Tables, careful interpolation being necessary in dealing with the incomplete integrals.

We write

$$y = \int_0^\infty \cos^2\theta\, d(\beta^2) = \int_0^1 \cos^2\theta\, d(\beta^2) + \int_1^\infty \cos^2\theta\, d(\beta^2).$$

The first integral, putting $\beta^2 = \cos 2\gamma$, is equal to

$$2\int_0^{\frac{\pi}{4}} \cos^2\theta \sin 2\gamma\, d\gamma,$$

and the second integral, putting $2\beta^2 = \sin\alpha + \operatorname{cosec}\alpha$, is equal to

$$\frac{1}{2}\int_0^{\frac{\pi}{2}} \frac{\cos^3\alpha}{\sin^2\alpha}\cos^2\theta\, d\alpha.$$

The intervals in the numerical integration for γ were taken at 2° from 4° to 45°, and those for α at 4° from 4° to 80°. At the limits of the integrals special precautions had of necessity to be taken, and the corresponding series for the elliptic integrals had to be used.

As regards the calculations of the first type ($z\lambda > 1$) the real difficulty arises when $\beta > 1$, and $\frac{\pi}{2} > \alpha > \epsilon$. It was found best to take ϕ_1 defined by (16) as the independent variable, so that

$$\int_{\epsilon}^{\frac{\pi}{2}} \cos^2\theta \frac{\cos^3\alpha}{\sin^2\alpha} d\alpha = \frac{1}{\sin\epsilon} \int_{\phi_0}^{\frac{1}{2}\pi} \cos^2\theta \sin^2\phi_1 \left(1 - \frac{\sin^2\epsilon}{\sin^4\phi_1}\right) d\phi_1,$$

where

$$\sin\phi_0 = (\sin\epsilon)^{1/2}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In carrying out the numerical integration for y, Weddle's rule for six equal intervals was used, and also the method of differences*. It was found that Simpson's rule was quite unreliable if 5 figure accuracy was to be aimed at in the value of y.

The results of the calculation for y for $z\lambda \leq 1$ were as follows :—

TABLE I.

$z\lambda \rightarrow$.	0.	$\frac{1}{16}$.	$\frac{1}{8}$.	$\frac{1}{4}$.	$\frac{1}{3}$.	$\frac{1}{2}$.	$\frac{3}{4}$.	1.
y ($\beta<1$)	·44893	·42396	·41321	·39869	·39173	·38176	·37360	·37046
y ($\beta>1$)	·10366	·10366	·10366	·10366	10366	·10366	·10366	·10366
y	·55259	·52762	·51687	·50235	·49539	·48542	·47726	·47412

For $z\lambda \geq 1$ the values of y are given in Table II.

TABLE II.

$z\lambda \rightarrow$.	1.	1·155	1·333	2.	3.	4.	6.	8.
y ($\beta<1$)	·37046	·37050	·39471	·53632	·67620	·75377	·83457	·87543
y ($\beta>1$)	·10366	·10079	·08046	·03560	·11354	·27105	·68313	1·13747
y	·47412	·47129	·47517	57192	·78974	1·02782	1·51750	2·01290

* *Cf.* D. Gibb, 'Interpolation and Numerical Integration,' Edinburgh Mathematical Tracts, No. 3.

In the final calculation of Y from (12) two methods were available, either to choose a series of values of λ and then to use numerical integration, or to try to express the results in Tables I. and II. in algebraic form, and then to use tables of Gamma functions for the final integration. The second method was adopted in order to avoid lengthy tabulations, and it did, I think, justify its choice.

If we write t for $z\lambda$, the entries in each table have to be taken in two portions, giving the following expressions :—

$(0 < t \leq \frac{1}{4})$, $y = 0{\cdot}55259 - 0{\cdot}10236t^{\frac{1}{2}} + 0{\cdot}00376t$,

$(\frac{1}{4} \leq t < 1)$, $y = 0{\cdot}53180 - 0{\cdot}14784t + 0{\cdot}13016t^2 - 0{\cdot}04000t^3$,

$(1 \leq t \leq 2)$, $y = 0{\cdot}66029 - 0{\cdot}32816t + 0{\cdot}14199t^2$,

$$(2 \leq t < \infty), y = \tfrac{1}{4}t + \frac{0{\cdot}10014}{t} + \frac{0{\cdot}17487}{t^3}.$$

The approximation $\frac{1}{4}t$ corresponding to the case of elastic collisions is a useful check on the values of y for large values of t.

Finally, the values of λ were taken at intervals of 0·1 from 0 to 4, and the integrals were calculated by means of Karl Pearson's Tables of the Incomplete Gamma Function. The results are given in Table III.

The errors in the calculation of A arise from the expressions for y as algebraic functions of t for certain ranges of the latter variable. These errors are estimated to be possibly as much as 1 in 1250 for the range $0 \leq t \leq \frac{1}{4}$, 1 in 700 for the range $\frac{1}{4} \leq t \leq 2$, and 1 in 6000 from $t = 2$ onwards. The resulting error in A is then calculated to be less than 1 in the third place of decimals from $\lambda = 0{\cdot}1$ to 1·1, and to be less than 1 in the fourth place of decimals for values of $\lambda \geq 2$.

The curve of A as a function of λ follows that given by Langevin very closely, and confirms the existence of a maximum value at about $\lambda = 0{\cdot}6$ for which there does not appear to be any obvious physical interpretation. It indicates that when $(K - 1)$ is given, there is a certain value of σ for which the mobility is a maximum. On the other hand, Table III. shows that λA increases steadily to the limiting value 0·75, so that when σ is given the mobility (*cf.* eqn. (7)) steadily increases as the effect of the attractive forces diminishes, as we should expect.

It is interesting to note that the expansion of A in the neighbourhood of its value when $\lambda = 0$ is

$$A_0 + B\lambda^{\frac{1}{2}} + \ldots\ldots,$$

so that $dA/d\lambda$ is infinite when $\lambda = 0$.

TABLE III.

λ	A.	Aλ.	λ.	A.	Aλ.
0·0	·5105	·0000	2·1	·3370	·7077
0·1	·5488	·0549	2·2	·3236	·7119
0·2	·5648	·1130	2·3	·3111	·7155
0·3	·5756	·1727	2·4	·2994	·7186
0·4	·5836	·2334	2·5	·2886	·7215
0·5	·5886	·2943	2·6	·2784	·7238
0·6	·5904	·3542	2·7	·2689	·7260
0·7	·5878	·4115	2·8	·2599	·7277
0·8	·5796	·4637	2·9	·2515	·7293
0·9	·5662	·5096	3·0	·2436	·7308
1·0	·5483	·5483	3·1	·2362	·7322
1·1	·5277	·5805	3·2	·2292	·7334
1·2	·5057	·6068	3·3	·2226	·7346
1·3	·4834	·6284	3·4	·2163	·7354
1·4	·4614	·6460	3·5	·2104	·7364
1·5	·4402	·6603	3·6	·2048	·7373
1·6	·4201	·6722	3·7	·1994	·7378
1·7	·4011	·6819	3·8	·1944	·7387
1·8	·3834	·6901	3·9	·1895	·7391
1·9	·3668	·6969	4·0	·1849	·7396
2·0	·3514	·7028			

It is of interest to see how far Sutherland's formula, which applies only to weak attractive forces, is in error in this case, which corresponds to the diffusion of one gas into another when the molecules are spheres with a surrounding field of attractive force, varying inversely as the fifth power of the distance. The expression for A in our notation is *

$$\frac{3}{4\lambda}\frac{1}{[1+0\cdot2011/\lambda^2]} \quad . \quad . \quad . \quad . \quad (18)$$

For example, $\lambda = 2$ gives $A = \cdot3562$ instead of $\cdot3514$, $\lambda = 2\cdot5$ gives $\cdot2907$ instead of $\cdot2886$, and $\lambda = 3$ gives $\cdot2445$ instead of $\cdot2436$. Thus Sutherland's approximation is in error by less than 1 per cent. for $\lambda = 2\cdot5$, and by less than 1·4 per cent. when $\lambda = 2\cdot0$. Further, the values calculated from James' formula are all in excess of the correct values in accordance with his result that the next term in the series in λ^{-2} in the denominator of (18) is positive.

* *Cf.* James, *loc. cit.* p. 454.

III. Application to the Calculation of Mobilities.

1. *Physical Data of the Theory.*

The quantities on which the theoretical determination of the mobility of an ion depends are the distance σ between the centres of the colliding ion and molecule, the masses M and m, the density ρ of the gas, and the value of $K-1$ for the gas. There is a fair measure of agreement in the results given by different methods for the statical value of $(K-1)$, which has been taken for a temperature of 15° C. The values of the density ρ have been taken from Kaye and Laby ('Physical Constants,' p. 26), and have similarly been reduced to a temperature of 15° C. These values are given in the following table:—

Table IV.

Gas	$(K-1)\times10^6$ at 15° C.	$\rho\times10^3$(gms./cm.^{3}) at 15° C.
Air	543	1·226
Argon	529	1·688
Helium	66	0·1689
H_2	250	0·0852
O_2	491	1·355
CO	656	1·185
CO_2	898	1·875
NH_3	7450	0·7306
SO_2	8760	2·774

In order to determine the value of σ, we must know the values of the radii s and s' of the molecule and ion respectively, and this involves a definite assumption as to their constitution. The most general procedure would be to consider a neutral molecule as the seat of both repulsive and attractive forces, and to consider in addition the attractive forces between the ion and the neutral molecule. Unfortunately the theory as at present developed does not allow of such a general treatment. The method of simplifying the problem that immediately suggests itself is to take the repulsive force as equivalent to that given by collision with an elastic sphere of radius s_0, the so-called "kernel" of the molecule. We are then left with the attractive force due to cohesion, and that due to the electrical field of the charged ion, and here again the proper method is to combine these into a single attractive force, and to separate out the

constituent parts in the application to any particular case. This method, due to Sutherland, has difficulties of its own of a mathematical character, and must be left over for further consideration.

Another possible method is to take the effect of the attractive and repulsive forces of the neutral molecule as equivalent to that given by an elastic sphere of radius s, determined from measurements of viscosity, and given by Jeans * for a temperature of 0° C. This method is clearly very unsatisfactory and most of the difficulties we shall meet with may be traced to its use, but it is the best that can be adopted in the present state of our knowledge, and these values of the radius s of the molecule will be used in the numerical calculations given in this paper. The value of s will depend on the temperature, and the value taken in all cases is that corresponding to a temperature of 15° C., since the values of $(K-1)$ and ρ have also been taken for this temperature.

The effect of the attractive force between the ion and the neutral molecule given by (4) is then calculated from Langevin's theory as an effect superposed on that due to the attractive and repulsive forces of the molecule itself. This is a further definite assumption, and one which it is impossible to justify, either physically or mathematically. There appears to be no reason why the effect of the collision of a charged and a neutral molecule should be represented by the same value of the "effective" radius s as in the case of the collision of two neutral molecules.

We are now in a position to calculate the value of λ from (6), and to determine the mobility from (5), in which the numerical values must be divided by 300 in order to express the results in cm./sec. per volt/cm.

2. *Mobility of a Mono-Molecular Ion.*

The first case we shall consider is that in which the ion is a single molecule, positive or negative, when $M = m$, so that

$$k = \frac{A\sqrt{2}}{\sqrt{\rho(K-1)}}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where we have taken no account of the Chapman-Enskog correcting factor, and we shall then have the fo owing table :—

* Jeans, 'Dynamical Theory of Gases,' 3rd edition, p. 288.

TABLE V.

Mono-Molecular Ion.

Gas.	λ.	A.	*k*.
Air	·626	·590	3·41
Argon	·605	·590	2·95
Helium	·622	·590	26·6
H_2	·490	·588	19·0
O_2	·614	·590	3·38
CO	·580	·590	3·16
CO_2	·733	·585	2·12
NH_3	·221	·567	1·15
SO_2	·331	·578	0·545

These values are far larger than those given by the experiments, and of course there is no difference in the mobility of the positive and negative ion on this assumption of a single mono-molecular ion.

According to this theory these are maximum values for the mobility. If the higher values obtained in some experiments are substantiated, there must be free electrons present, and the higher mobilities must be due to stable concentrations of electrons and molecules in different quantities.

3. *Mobility of a Clustered Ion in its own Gas.*

It has therefore been suggested that the smaller mobility of the ion is due to the fact that the molecules form a cluster round the ion, and that we have to deal with the diffusion of the clustered ions in the field of the other molecules. The condition that such a clustering shall take place is that the potential energy of the molecule in contact with the ion shall be greater than the average kinetic energy of their relative motion. The ratio of these two energies is

$$\frac{(K-1)e^2}{8\pi N\sigma^4}\Big/\left(\frac{3}{2}kT\right)=\frac{(K-1)e^2}{12\pi p\sigma^4}=\frac{2}{3\lambda^2},$$

where k is the ordinary gas constant *.

The ratio $2/3\lambda^2$ may be called the clustering coefficient, and we see that it will be greater than unity if λ is less than 0·8165, which is the case for all the gases given in Table V.

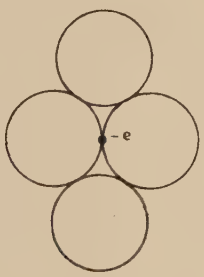
* It should be realized that this deduction of the condition of clustering belongs to a different order of ideas from that of strict kinetic theory. According to the latter there can be no such clustering, as two molecules or ions will always separate after an encounter. Hence those conclusions given in this paper which depend on this clustering condition may be liable to modification.

The positive ion will then be represented, following Langevin, as a sphere of radius s with a layer of spheres, 12 in number, clustered round it. This makes $M = 13m$, and the distance σ between the centres of a molecule and the clustered ion at collision is then practically $4s$, though the average distance would be slightly less than this.

It is more difficult to form a satisfactory representation of a clustered negative ion. Assuming that the basis of the cluster is a free electron, Langevin takes the clustered ion as a sphere of radius $2s$, so that $\sigma = 3s$, and takes the masses of the molecule and ion as proportional to their volumes, which makes $M = 8m$.

It is desirable for certain purposes to make this representation more definite, and we may suppose that initially two molecules will attach themselves to the free electron, forming two spheres in contact, and that further molecules, 5 in number, will cluster round these two in their plane of symmetry, as in the figure representing a section of the cluster.

Fig. 1.



In this case $M = 7m$, and the average radius of this cluster can be calculated by the methods introduced by Rankine*, taking the cluster as equivalent to an ellipsoid of revolution, and calculating its mean collision area.

In the remainder of this section we shall consider the case of an ion in a gas composed of its own molecules. The cluster is therefore formed of these molecules, and the collisions of the clustered ion are with other molecules of the gas. The results may therefore be taken as applying to a dry gas only ; the effect of the presence of water vapour will be considered in the next section.

* Rankine, Proc. Roy. Soc. A, xcviii. p. 360 (1921).

The following table gives the results of calculation as applied to the positive ion :—

TABLE VI.

Positive Clustered Ion.

Gas.	λ.	A.	k.
Air	2·504	·288	1·37
Argon	2·420	·297	1·23
Helium	2·488	·290	10·8
H_2	1·960	·358	8·45
O_2	2·456	·293	1·40
CO	2·320	·309	1·37
CO_2	2·932	·259	0·78
NH_3	0·884	·568	0·84
SO_2	1·324	·478	0·33

It will be seen that the values of λ are all greater than 0·816, so that no further clustering will take place.

It should also be noticed that in most of the cases the value of λ is so large that equation (8) is applicable, so that the mobility is independent of the value of $(K-1)$, and it could have been calculated directly from this equation. Hence, in the case of positive ions, the attractive forces are instrumental in forming the cluster, the mobility of which depends then largely on its radius.

TABLE VII.

Negative Clustered Ion.

Gas.	λ.	A.	k (Langevin's Representation).	k (Cluster as in fig. 1.)
Air	1·408	·460	1·99	2·04
Argon	1·363	·469	1·76	1·79
Helium	1·400	·461	15·6	16·1
H_2	1·102	·527	12·7	13·0
O_2	1·382	·465	2·02	2·07
CO	1·305	·482	1·93	1·98
CO_2	1·649	·411	1·11	1·14
NH_3	0·497	·588	0·89	—
SO_2	0·745	·584	0·41	—

We may in a similar way calculate the mobility of a clustered ion, and here it is of interest to give some results, both for Langevin's rough representation, and for the more

definite clustering shown in fig. 1. It will be seen that these differ very slightly, a result which may be taken as suggesting that the geometrical form of the cluster will have very little effect on the mobility, which naturally gives a statistical average over a large number of clusters.

Theoretically, further clustering should take place in the case of NH_3 and SO_2 since $\lambda < 0{\cdot}816$, but it is not worth while to deal with these cases in further detail. The values of k correspond to the values of λ given in the table.

Other possibilities in the way of representing the geometry of a clustered negative ion obviously suggest themselves, but it is hardly desirable to consider them at this stage of the inquiry.

IV. Comparison with Experiment.

1. *Mobilities of Ions in Dry Gases.*

The results given in the previous section relate to fully-clustered ions, and cannot therefore be taken as applying to experiments intended to give values for the mobility of partially-clustered ions which correspond to a position of minimum energy, but not in a state of greatest stability.

We have the following results, in which the calculated values for the mobilities of positive and negative ions, denoted by $k+$ and $k-$ respectively, are taken from Tables VI. and VII. :—

Table VIII.

Positive Clustered Ion.

Gas.	$k+$ (Theoretical).	$k+$ (Experimental).
Air	1·37	1·40, mean value, Kaye and Laby, p. 95.
Argon..	1·23	1·37, Franck (1910).
elium	10·8	5·09, Franck and Pohl (1907).
H_2	8·45	5·4, Haines (1916); 5·33, Lattey and Tizard (1912); 5·8, Chattock and Tyndall (1910).
O_2	1·40	1·33, mean value, Kaye and Laby.
CO	1·37	1·10, Wellisch (1909).
CO_2	0·78	0·82, mean value, Kaye and Laby.
NH_3	0·84	0·74, Wellisch (1909).
SO_2.	0·33	0·44, Wellisch (1909).

TABLE IX.

Negative Clustered Ion.

Gas.	$k-$ (Theoretical).	$k-$ (Experimental).
Air	1·99	1·78, mean value, Kaye and Laby; 2·15, Loeb (1923).
Argon	1·76	1·70, Franck (1900).
Helium	15·6	6·31, Franck and Pohl (1907).
H_2	12·7	7·9, Haines (1916); 8·12, Lattey and Tizard (1912); 7·6, Chattock and Tyndall (1910).
O_2	2·02	1·82, mean value, Kaye and Laby.
CO	1·93	1·14, Wellisch (1909).
CO_2	1·11	1·01, Kovarik (1910); 1·05, Lattey and Tizard (1912).

The agreement in both cases is fairly satisfactory, except in the case of the light gases Helium and Hydrogen. It is, indeed, more satisfactory than we have a right to expect, considering the nature of the assumptions made in the course of the calculation. In view of the disagreement in the case of the light gases, it is possible that such agreement as there is in the other cases may be quite accidental.

2. *The Effect of Water Vapour.*

It has been suggested that, since free electrons are present in many of the gases considered above when in a highly purified state and these would naturally have very high mobilities, the experimental values given above for negative ions are really the mobilities of water-vapour clusters in the presence of the molecules of the gas itself. It is of interest to consider this question on the basis of the method of calculating mobilities given in this paper.

Assuming such a cluster is possible, we require for the calculation of the mobility the value of the effective radius s of a water-vapour molecule. Taking the value 97×10^{-6} c.g.s. units for the viscosity of water vapour at 15° C., as given in Kaye and Laby, p. 31, which agrees well with more recent values, we find that $s = 2{\cdot}24 \times 10^{-8}$ cm.

In the case of Air it is then found that if the ion is clustered with water-vapour molecules instead of air molecules, the value of $k+$ is reduced from 1·37 to 1·15, and the value of $k-$ from 1·99 to 1·68. In the case of H_2 the presence of water vapour in sufficient quantities to allow of the formation

of clusters of water vapour round the H_2 ions will make the mobility of the positive ion in H_2 equal to 4·85, and that of the negative ion equal to 7·37, so that the suggestion does lead to better agreement between theory and experiment in this case.

Unfortunately, the same is not true in all cases. The mobility of an ion in slightly damp gas, so that it is clustered with water-vapour molecules, in the presence of molecules of its own gas as compared with the mobility in dry gas, depends according to the method of calculation only on the difference in values of the radii s of a water-vapour molecule and that of a molecule of the dry gas. Hence, in the case of CO_2, where s has the value $2{\cdot}31 \times 10^{-8}$ cm., and is therefore greater than the radius of a water-vapour molecule, we should expect a decrease in mobility when the gas is dried, which is contrary to the experimental results.

3. *Mobilities of Ions in Foreign Gases.*

The important experimental fact that the mobility of the positive ion depends only on the gas into which it is introduced has already been mentioned in I. 2 above, and has been used there to show the necessity of a cluster. If this is so, and the recent experiments of Tyndall and Grindley * seem to leave very little room for doubt on the point, then, as has been shown by J. J. Thomson † in connexion with the limiting cases of Langevin's theory discussed by him, it leads to conclusions which are of great theoretical significance. From the general formula (5) it follows from this experimental result that A must be independent of the nature of the ion. Since A is a function of λ, then either A must vary very slowly with λ, or else σ must be practically the same for all ions clustered with molecules of the same gas. The first possibility means that A must have values near its maximum, which corresponds to $\lambda = 0{\cdot}6$ approximately, and this would mean according to the theory that further clustering would take place. Hence it follows that the radius of an ion fully clustered with molecules of a given gas must be practically independent of the nature of the ion.

The method of calculating the mobility as used in this paper leads to results quite at variance with the experimental fact we are considering. Thus, in the experiments of

* Tyndall and Grindley, Phil. Mag. xlviii. p. 711 (1924).

† J. J. Thomson, *loc. cit.*

Tyndall and Grindley referred to, a CO_2 ion and a H_2 ion in air are shown both to have the same mobility as that of an air ion in air. Assuming a cluster of air molecules in each case the values of σ (*cf.* Jeans, *op. cit.* p. 288) are in the ratios $2{\cdot}31+3\ (1{\cdot}87) : 1{\cdot}36+3\ (1{\cdot}87) : 1{\cdot}87+3\ (1{\cdot}87)$ or $7{\cdot}92 : 6{\cdot}97 : 7{\cdot}48$ in the three cases. Since the value of λ is large, equation (8) is applicable, and it follows that the substitution of a CO_2 ion for an air ion lowers the mobility in the ratio $(7{\cdot}92)^{-2}$ to $(7{\cdot}48)^{-2}$ or 0·89, and that the substitution of a H_2 ion will raise it in the ratio 1·15. These differences of 11 and 15 per cent. are quite outside the possible errors of the experiment.

V. General Discussion of the Theory.

The considerations given in IV. 2 and IV. 3 show that, in spite of the results of IV. 1, the method of calculating the mobilities is not very satisfactory. It is clear, in fact, that we cannot use the "effective" radius s of the molecule for this purpose. The fields of force which are represented by this radius will interpenetrate, and will possibly be altered in magnitude, owing to the additional attractive force exerted by the ion on the molecule, and it will be necessary to find some means of determining the size and shape of the clusters before much progress can be made.

It is possible that the fields will interpenetrate so much that the clustering is of a more extensive character than that so far contemplated. This would result in the size of the cluster being practically independent of the size of the ion at its centre, but a numerical estimate will have to be provided before any definite statement can be made.

The above remarks do not apply to the calculated values for the mobility of a mono-molecular ion given in Table V., since there is no question of any clustering in this case, so that the numbers given there remain the estimated maximum values.

In this connexion it is important to realize the limitations of the theory of mobility as given in this paper. No attempt has been made to consider in detail how the clustering takes place, or what types of cluster are likely to occur; nor does the theory necessarily apply when there are free electrons present, as has been at times suggested in order to account for certain experimental results. A discussion of some of

these questions from the theoretical side has been given by J. J. Thomson *, based on the ideas associated with the older type of kinetic theory.

For example, the experiments of Erikson † have shown that there are two types of positive ion, an initial ion of about the same mobility as the negative ion, and a final ion of much smaller mobility. The only way of accounting for this fact on the present theory would appear to be to assume that initially the positive cluster is of the same type as that given in fig. 1, in which $+e$ takes the place of $-e$ in the figure, and that this cluster changes into one in which the positive ion becomes the centre of a group of molecules surrounding it. The theory does not enable us to say why these two types of ion exist. Erikson's explanation, since it is based on Wellisch's equations for the mobility, cannot, for the reasons given in I. 2 above, be considered satisfactory.

Again, in the case of the negative ion, some evidence has been given of the existence of mobilities higher than that calculated above in III. 3. We may therefore consider in the case of Air what would be the mobilities of negative ions obtained by building up ions of one, two, ... molecules in succession. The mobility of the mono-molecular ion is 3·41, while that of the fully-clustered ion is 1·99. Other values are obtained by considering the possible geometrical representations of partially-clustered ions. The case of two spheres which touch and have the electron at their point of contact gives a value for the mobility of 2·85, while that of three spheres touching each other and having the electron at their geometrical centre makes the mobility equal to 2·43. The case of four spheres touching each other, and therefore having their centres at the corners of a tetrahedron, leads to the value 1·90, almost the same as that of a fully-clustered ion.

It is not desirable to place any great emphasis on these numerical values for the reason given at the beginning of this section, and owing also to the rough representation of clustered ions on which they are based. They have been added here in order to complete the review given in this paper of the relation of the results of this method of calculating mobilities to the results given by experiment.

* J. J. Thomson, Phil. Mag. (6) xlvii. p. 337 (1924).
† Erikson, Phys. Rev. xx. p. 117 (1922).

Summary and Conclusions.

1. The paper has been written in order to recall attention to the theory of ionic mobility given by Langevin in 1905, and to consider the applications of the theory to problems in this subject. This is the only theory of mobility which is satisfactory from a theoretical point of view, since it is based on the rigorous mathematical investigations introduced into the kinetic theory of gases by Maxwell and Boltzmann.

2. A recalculation has been given of the numerical portion of Langevin's paper. This confirms the existence of a maximum mobility for a particular value of the distance between the centres of the ion and molecule at collision, the magnitude of the attractive forces being given.

3. Calculations of the mobility of several gases at atmospheric pressure are made on various assumptions, more or less reasonable, as to the size and shape of the molecules and clusters involved.

4. It is shown that the application of the theory as at present developed fails to account for some of the more fundamental experimental results, in particular for the fact that the mobility of a positive ion depends only on the nature of the gas through which it is diffusing under the influence of the external field.

5. The paper is therefore mainly of the nature of a preliminary investigation, and further work will be necessary before the application of the theory to the calculation of mobilities and the comparison of the results with experiment can be dealt with in a satisfactory manner.

My thanks are due both to Dr. J. E. Lennard-Jones, who is working on the subject from another point of view, and to Prof. A. M. Tyndall, with whom I have had the opportunity of discussing certain points connected with the theoretical and experimental side of the subject respectively.

In connexion with the numerical work of Section II., I should like to acknowledge the valuable assistance I have received from Miss D. L. Holland and Miss N. M. Hunt.

The University of Bristol.
August 1925.

XI. *Mechanical Models for the Zeeman Effect.* By C. G. Darwin, *M.A., F.R.S., Tait Professor of Natural Philosophy in the University of Edinburgh* *.

Abstract.

The field of applicability is discussed of mechanical models for spectral lines (§ 2).

The principles are explained (§ 3) and the actual form is given (§ 10, 11) of a simplification of Voigt's model of the D lines, which invests it with much greater physical significance.

A curious theorem is found concerned with the magnetic gyration of light (§ 8). Provided the assumed type of model is correct, the gyration of light of frequency far distant from the lines of a multiplet should correspond to a normal Zeeman effect, and should show no trace of the anomalous effect no matter how weak the field or how complex the multiplet.

It is shown (§ 9) that some types of multiplet cannot be represented by the simple form of the model.

An attempt is made to construct a model for the triplet (§§ 14–15). The result satisfies all the known properties, but no success has been attained in finding a simple form such as would suggest a basis of physical reality.

The remaining sections are concerned with technical principles of the theory of vibrations.

In spite of the rather striking success with the doublet, the general verdict seems probable that though models can always be devised for any type of line, they will not in general possess the simplicity which would make them useful.

1. *Introduction.*

In the last few years the theory of the Zeeman effect has undergone enormous developments with the help of quantum principles, and it is hardly too much to say that the position and intensity of every line are now completely known. But there remains outstanding the question of how a substance will react to light of frequency different from its own lines. In dealing with the refraction and magnetic rotation of light our guiding principle is the Lorentz theory of electrons, and to use this we must have some sort of mechanical model for the atom. In addition to the simple elastically bound electron of Lorentz, there exists one other model

* Communicated by the Author.

which was devised by Voigt* to describe the behaviour of the D lines of sodium. It seemed to me that, in view of the greatly increased knowledge we now possess, it would be worth while to re-examine the subject and to see whether other models of the same type could be usefully made. The principles of which we shall treat were I think mostly contained in Voigt's own work, but in some respects he was aiming in wrong directions through insufficient experimental information. Moreover, there is no avoiding the fact that Voigt's papers make exceedingly difficult reading, and it may be doubted if they have been much studied for that reason ; so a new development of the theory may have some value.

To use a mechanical model at all we must, of course, have some connecting link between the classical and the quantum theories. Though the underlying principles are still quite unknown, such a link can be made in a manner described by Ladenburg † and later and with a fuller theory by Kramers ‡. With these rules it is quite possible to calculate the dispersion of any light passing through a substance, when we know the frequencies, intensities, and polarizations of the lines it emits in any strength of magnetic field ; but Voigt's model can do much more than this, for it can derive from a fairly simple set of equations the whole behaviour of the spectrum for both weak and strong fields. In the course of the present work it was found that Voigt's model could be cast into a much simpler form, and one in which a good deal of physical significance could be seen. This gave a new direction to the work, for it seemed that the same might be possible for other types of multiplet. I am rather inclined to think that this is not so, and that it is an accident that Voigt's model embodies so many facts in such a small compass, but the algebra becomes so involved and the number of alternative choices so vast that it is by no means possible to be certain. I had the impression in starting the work that it would not be easy to find any systems which would accommodate all the known facts, for example, the behaviour in both weak and strong fields. It soon appeared, however, that the opposite would be the difficulty ; the condition for the Paschen-Back effect takes a simple and indeed rather elegant form, but is quite insufficient to determine many of the

* Voigt, *Ann. der Phys.* vol. xli. p. 403 (1913), and vol. xlii. p. 210 (1914). Voigt's model is fully discussed by Sommerfeld, *Z. f. Ph.* viii. p. 257 (1921).

† Ladenburg, *Z. f. Ph.* vol. iv. p. 451 (1921).

‡ Kramers, 'Nature,' vol. cxiii. p. 673, and vol. cxiv. p. 310 (1924).

constants of the model. Before proceeding to the detailed theory, we must review the general question of the possibility of representing the facts of optics by means of mechanical models.

2. *The General Applicability of Mechanical Models.*

We are going to deal with ordinary vibrating systems and must first examine in general terms how far we may hope that they will be able to represent the facts of physics. The four main effects to be examined are dispersion (including magnetic rotation), emission, absorption, and resonance radiation, and we are starting from the opposite end from that done by the quantum theory, in that we take our system to give the dispersion correctly and then see how it will deal with the other phenomena. Since all dispersive effects are independent of intensity the equations of motion of the model must be linear, and come under a fully known theory. The model is necessarily somewhat unnatural in that, to represent a multiplet, it must have a considerable number of nearly equal frequencies. Though it is not easy to conceive of a real atom having this property, yet it does free us of one of the objections to mechanical models for spectra ; for by taking the differences between the frequencies as small, we can get period equations which are linear in the frequency (and not quadratic as in the general case) and so can much more easily fit the system to the linear expressions for the frequency that occur in the quantum theory. Furthermore, this approximation very considerably simplifies the theory of the vibrations of systems containing gyroscopic terms. The model must not only have the correct natural frequencies, but each of these must have the correct "force factor," so as to describe their relative importance in reacting to the incident light.

When the model has been chosen to fit the dispersion, we have to consider what spectrum it will *emit*. The most usual way of exciting the emission of radiation is by means of electron collisions. The process is essentially one of which the quantum theory gives a good and the classical theory a bad account, and so we cannot expect that our model will represent the event very successfully. We suppose that the impact of the electron gives the various degrees of freedom certain displacements and velocities, and that it then describes free vibrations. The dispersion theory then determines the emission. In general the strengths of the various lines will depend on the initial values chosen, and we conclude that there is not, in general, a definite set of

ratios for the intensities of the members of a multiplet. We may note that there is an analogous theorem in the quantum theory. For example, the impinging electrons might all have enough energy to excite D_1 but not D_2, and we should then certainly not observe the usual ratio 1 : 2. We expect that the electron velocities must be a good deal higher before this ratio is given. Taking the analogy back again, we shall show that our model will give a perfectly definite set of ratios—that determined by the dispersion—provided that there is an equipartition of energy among the degrees of freedom of the model. The question of the intensity ratios for lower velocities of impact is most interesting, but falls outside our present subject. We may note that for temperature radiation the quantum theory gives a perfectly definite answer, which will usually not be far from that given by equipartition : the conditions in a discharge tube defy precise analysis, but the velocities of the electrons are usually so high as to give practical equipartition.

If the only damping of the vibrations is due to the re-emission of electromagnetic waves, it follows by a purely thermodynamic argument that the intensity of absorption must equal that of emission. We shall see, however, that for resonance radiation some other type of damping is needed, and we are then confronted with a problem in which the balance of energy is not explicitly maintained. We shall show that whatever the damping factors, provided they are small, the absorption will follow the same rule as dispersion and emission. We shall not consider the question of the breadths of the spectral lines, and so there is no need to inquire deeper into the matter.

The question of resonance radiation is more difficult and falls more distinctly outside the competence of the classical theory. The crudest form of analogy would suppose that the incident light, having the same frequency as the natural frequency of the model, would set it into strong vibration in a phase determined by the electromagnetic damping of the model, and that the resonance radiation was the light scattered in the process. This will not do at all. For when light is scattered in this way the waves from the separate atoms are all in phase together (though perhaps out of phase with the incident light) and so the light scattered laterally is akin to the light of the sky, the intensity of which can be calculated directly from the refractive index of the air. To obtain the intense effect observed in resonance the vapour would have to have an enormous refractive index. There is no reason in the theory of dispersion why it should not have this large

index (real or complex), but that it does not is proved by the fact that there is no very strong reflexion from the surface of the vapour.

The only alternative to account for the strong scattering is to suppose that the atom is responsible for two waves. The first bears a definite phase relation to the incident of such a type that this is gradually extinguished in passing through the vapour. If this wave is associated with the ordinary electromagnetic damping factor it will represent no accumulation of energy in the atoms. To absorb energy the atom must have a further damping factor, and we must suppose that the strong scattering is produced when the atom discharges this energy at a later time and with arbitrary phase. It will be seen that this argument, though involving nothing but pure wave theory, points definitely towards the quantum way of regarding the matter, and we are forced to conclude that our mechanical model will fail to connect at all closely the absorption and the re-emission. This is confirmed by the fact that the resonance often gives rise to lines different from the exciting line, and these are immediately explained by the quantum theory. The only way of arriving at a construction for the process is to take a model having non-linear equations of motion. This will give wrong results for dispersion since the motion will not be directly proportional to the amplitude of the exciting force, and we must therefore expect that a new application of the Correspondence Principle will be necessary in order to interpret it *. I shall not here speculate further on the subject, for a paper evidently dealing with the matter is promised shortly by Kramers and Heisenberg †.

To make use of our more limited model we must assume that the energy is absorbed in a manner that would be indicated by the dispersion—there is no need to investigate precisely the damping coefficient unless we intend to study the breadth of the spectral lines etc.—that there is some sort of reorganization in the atom, after which the energy is re-emitted, but to decide the reorganization we have to invoke the quantum theory. For example, we must simply take it as given that in sodium the excitation of $1s$–$2p_1$ leads to a re-emission of that line only, while in thallium $2p_1$–$1s$ leads

* It is tempting to compare the two waves with the superposed forced and free vibrations of a system starting from rest, but the correspondence must be more complicated than this for the solution of a set of non-linear equations does not divide up into two parts in this way.

† This paper has since appeared, *Z. f. Ph.* vol. xxxi. p. 681 (1925); it is an amplification of Kramers's work (*loc. cit.*).

to a re-emission of that line accompanied by $2p_2$–$1s$, the intensity ratio being that given by the dispersion. So we must suppose that as a result of quantum arguments our model acquires certain initial values for its coordinates, and calculate the intensities from these.

3. *The Transformation of Voigt's Model of the* D *Lines.*

We shall now consider Voigt's model in general terms. He worked it out mainly by fitting it to the effect in weak fields; and found, it might be said almost by accident, that it fitted for strong fields as well. Also by taking his equations in as symmetrical a form as possible he obtained the intensities of the components in weak fields according to the following scheme :—

	D_2.			D_1.	
Frequency	$\pm\frac{5}{3}$	± 1	$\pm\frac{1}{3}$	$\pm\frac{4}{3}$	$\pm\frac{2}{3}$
Intensity	1	3	4	2	2
Polarization	$\perp$	$\perp$	$\parallel$	$\perp$	$\parallel$

In very recent developments of the quantum theory these intensities are accepted as correct; but there does not seem to be any direct verification of them from emission spectra. Until recently it was believed that the light was anisotropic and that the intensities of the components were much more nearly equal; and it is thus rather natural to take the fact that the model was ahead of theory as a confirmation of its objective reality. Though there has been no satisfactory measure of the intensities of emission, it should be observed that the values above were proved long ago by perfectly cogent though slightly indirect arguments based on the necessary connexion between refraction and emission. Thus every experiment on magnetic double refraction shows the birefringence to be proportional to the magnetic field, and this proves that the anisotropy of the atoms is also proportional to the field, and not absolute, as would be suggested by the crude form of the quantum theory. Further, the same type of argument will determine the intensities of the lines from their dispersive effect. This was done in some very fine experiments by Hansen*, and with an accuracy sufficient to verify the above values to 10 per cent. Thus Voigt's model fits in with present theory to a very complete degree. In only one respect can it be attacked.

* Hansen, *Ann. der Phys.* vol. xliii. p. 169 (1914).

Landé * has recently applied Heisenberg's† method of quantizing so as to find the position of the lines for intermediate fields, and his results definitely do not agree with Voigt's. There seems to be no conclusive experimental evidence on the point. As the physics of Heisenberg's process are incompletely understood, we cannot feel full confidence that it destroys the validity of the model, but, taken in conjunction with results that will be given later, it does look as if the success of the model were rather accidental. We shall next describe the general principles of the modifications which have improved its form.

As the atom cannot be really described at all in terms of ordinary mechanics there is no use in associating very precise physical meanings with the variables of the mechanical system which acts as model. A sufficient starting point will be to set down its Lagrangian function. This is composed of four parts: the first three, kinetic energy, potential energy, and gyroscopic terms, constitute a quadratic form in the coordinates and velocities. The fourth is the "force function," which describes the connexion with the outside world; it is a bilinear form in the coordinates and the external forces. Only if the model is of this form will the equations of motion be linear, as is required if the refractive index is to be independent of the intensity.

The usual problem of vibrations starts with a known form and requires us to find the natural frequencies of the motion and their modes. Here the question is the exact opposite; we know all the natural frequencies and their intensities, and our object is to discover a simple algebraic form which can be responsible for them. This was successfully done by Voigt, and his equations of motion have an attractive type of symmetry, but the Lagrangian function from which they are derived is a very long expression if written out in full. Now in treating of the ordinary problem of vibrations a certain degree of simplicity is obtained by first reducing the kinetic and potential energies to sums of squares, and then later studying the effects of the gyroscopic terms. This form of the expression may conveniently be called the *semi-normal*, and it would not be expected to be as significant as the original form or as simple mathematically. The semi-normal form is exactly what is used in describing the anomalous Zeeman effect in weak fields, for it refers each vibration to the value it would have if there were no gyroscopic terms. Voigt has his equations of motion in this

* Landé, *Z. f. Ph.* vol. xxx. p. 329 (1924).
† Heisenberg, *Z. f. Ph.* vol. xxvi. p. 291 (1924).

form. The first modification we shall make is to abandon it, by including product terms in the potential energy (or the kinetic), and we shall find that a great simplification results.

The second modification is quite as important, and concerns the *force function*. Voigt works with three electrons all reacting to the external field in the same way. Now the quantum theory suggests that in sodium one electron is mainly responsible for the spectrum, the rest only acting indirectly by perturbing it. Though the analogy can only be rather loose, this suggested the idea of taking only one of the degrees of freedom as affected by external electric forces and the result was found further to simplify the model. Moreover, there is direct evidence that this is a step in the right direction from some experimental work by Minkowsky *. He finds that the absolute refractive index of sodium vapour is given by the classical theory if each atom contains one electron of ordinary charge and mass, responsible for the whole of both D_1 and D_2 †.

These two ideas led to very pronounced simplifications in the model, modifications which seemed to give it a much more physical meaning, and it looked possible that similar models might exist for other multiplets. There is, of course, no obvious reason why there should exist any at all, but the conspicuous success with the doublet made it well worth while to examine other cases. There even seemed to be a faint chance of constructing a general model which should contain the quantum numbers as numerical coefficients in its Lagrangian function; the algebra of the classical systems, it is true, is rather complicated, but in the only known case it was exactly equivalent to the simple arithmetic of the quantum theory. In dealing with multiplets we have an important fact of which account should be taken in the model, and this is that an ordinary multiplet can be approximately described in terms of two parameters, the frequency of its centre of gravity, and a single constant determining all the intervals between the lines. For example, in a triplet $1s$–mp the intervals are approximately in the ratios 1 : 2, and the intensities as 1 : 3 : 5. The semi-normal form gives

* Minkowsky, *Ann. der Phys.* vol. lxvi. p. 206 (1921).

† The dielectric constant of Na is presumably due to a single electron, which must therefore be responsible for the whole principal series. There should thus be a small reduction to allow for the higher members of the series. Ladenburg (*loc. cit.*) shows that the dispersive effect of these lines is insignificant.

directly the frequencies of the components, and fails to bring out the arithmetical character of their intervals. It was this consideration, indeed, that suggested abandoning the semi-normal form for the doublet, though there it is not essential, as the frequencies of the two lines can themselves be taken as the two parameters. In all the work advantage is taken of the fact that the intervals between the lines are small compared with the frequencies; this simplifies the vibration theory a great deal. The great number of components in even a triplet makes it hard to see what course the search for a model ought to take; and I should say at once that I have not succeeded in finding any form that looks at all natural. There is too vast a field of possibilities to be certain that there is no such form, but it certainly does not offer itself readily (as it did for the doublet), and this fact, taken in conjunction with the failure of Voigt's model to agree with Landé's formula, I think rather suggests that the success of the doublet was accidental.

4. *Force Factors and Emission Functions.*

We shall now develop certain general properties of vibrating systems. These belong to a well-established theory; but the case we are considering turns out simpler than the most general case—itself not very familiar—and so deserves treatment here. We shall work throughout with the Lagrangian form (denoting any such form by the symbol L), as for the present problem nothing is gained by using the Hamiltonian.

We first examine the way in which the system reacts to the outside world. We intend to make use of the electromagnetic theory in the applications, but shall first discuss it with a greater generality, as the argument is simpler. Let the system have n coordinates $q_1, q_2, \dots q_n$. Add a further one q_0, which on the one hand is used to set the system in motion, and on the other, to observe its motion. Then we have

$$\mathrm{L} = \tfrac{1}{2}\Sigma_r\Sigma_s[a_{rs}\dot{q}_r\dot{q}_s - b_{rs}q_rq_s + 2c_{rs}\dot{q}_rq_s] \quad (r, s = 0, 1, 2 \dots n). \quad (4{\cdot}1)$$

Without loss of generality,

$$a_{rs} = a_{sr}, \quad b_{rs} = b_{sr}, \quad c_{rs} = -c_{sr}. \quad . \quad . \quad . \quad (4{\cdot}2)$$

An equation of motion is then

$$\sum_{s=1}^{n}(a_{rs}\ddot{q}_s + 2c_{rs}\dot{q}_s + b_{rs}q_s) = -(a_{r0}\ddot{q}_0 + 2c_{r0}\dot{q}_0 + b_{r0}q_0). \quad (4{\cdot}3)$$

If the system vibrates so that each coordinate is proportional to e^{ipt}, we define the expression on the right as Q_r, the external force on q_r, and have

$$\begin{aligned} Q_r &= -q_0(b_{r0}+2ipc_{r0}-p^2a_{r0}) \\ &= e_r q_0. \qquad \ldots\ldots\ldots\ldots \quad (4{\cdot}4) \end{aligned}$$

We call e_r the *force factor* for q_r. It is in general a function of p and is complex. Next consider emission. To observe this we study the motion of q_0. Its equation is

$$\begin{aligned} a_{00}\ddot{q}_0+b_{00}q_0 &= -\Sigma_1^n(a_{0r}\ddot{q}_r+2c_{0r}\dot{q}_r+b_{0r}q_r) \\ &= -\Sigma_1^n(b_{0r}+2ipc_{0r}-p^2a_{0r})q_r. \quad . \quad (4{\cdot}5) \end{aligned}$$

Throughout the present paper *we shall denote the complex quantity conjugate to any quantity z by the symbol $\tilde{z}$*. Then by virtue of (4·2)

$$a_{00}\ddot{q}_0+b_{00}q_0=\Sigma_1^n\tilde{e}_r q_r. \quad . \quad . \quad . \quad . \quad (4{\cdot}6)$$

The right-hand side represents the force which the system exerts on the test coordinate q_0, and so we can see the general form that emission must bear to absorption.

This is, of course, really one of the well-known reciprocal theorems of dynamics. Without going into details we can specialize it to deal with electromagnetic systems. We shall assume that the linkage is, in fact, solely dependent on the electric force, though more general cases could be as easily treated *. Then to any coordinate x_r, which need not represent the position of an electron, there will correspond a force factor e_r, so that the force on the coordinate x_r will be $e_r X$. Our theorem tells us that the external action of the system will depend on an *emission function* $\Sigma_1^n\tilde{e}_r x_r$. This is as much as we require for the present work. The most familiar case is, of course, that where e_r is the charge on an electron and so is purely real, and in this case $\Sigma_1^n\tilde{e}_r x_r$ is simply the electric moment; but the work gains symmetry by retaining the greater generality which obtains when x_r is not simply the position of an electron. The further details of emission, which we do not require, consist in constructing a Hertzian vector from the three components of the emission function and differentiating it to obtain the potentials and electric and magnetic forces.

* For example, if a magneton reacted to the external magnetic force, it would be as easy to construct its effect in emission on the same principles.

5. *The Free Vibrations of the System.*

We next study the motions of the system, and shall introduce the condition which applies to multiplet lines, that all the vibrations have approximately equal frequencies—more precisely that the square of the difference between any two frequencies is negligible compared with the square of the frequencies themselves. This condition assimilates the problem rather closely to the familiar problem of vibrations about a position of equilibrium. The main difference lies in the fact that we have to deal with complex quantities and, speaking loosely, it will appear that half the symbols in the various formulæ must be replaced by their conjugates. We shall only outline the required theorems since the details can be filled in by analogy with the simpler theory.

We suppose that the kinetic energy is reduced to the sum of squares. Then the complete L is

$$\tfrac{1}{2}\Sigma_r(\dot{q}_r{}^2 - p_0{}^2 q_r{}^2) - \beta p_0 \Sigma_r \Sigma_s b_{rs} q_r q_s + \omega \Sigma_r \Sigma_s c_{rs} \dot{q}_r q_s + \mathrm{F}\Sigma_r e_r q_r. \quad . \quad . \quad . \quad (5{\cdot}1)$$

Here β and ω are two parameters of which the squares are negligible beside p_0, F is a component of external force, and we can take

$$b_{sr} = b_{rs}, \quad c_{sr} = -c_{rs}. \quad . \quad . \quad . \quad . \quad (5{\cdot}2)$$

We form the equations of motion

$$\ddot{q}_r + p_0{}^2 q_r + \Sigma_s(2\beta p_0 b_{rs} q_s + 2\omega c_{rs}\dot{q}_s) = e_r \mathrm{F}.$$

To solve we first equate the right-hand side to zero and put all coordinates proportional to $e^{i(p_0+\kappa)t}$, so that $p_0+\kappa$ will be a frequency of emitted light. Approximating with κ small of the order of β and ω, we have

$$-\kappa q_r + \Sigma_s(\beta b_{rs} + i\omega c_{rs}) q_s = 0. \quad . \quad . \quad . \quad (5{\cdot}3)$$

Put $\beta b_{rs} + i\omega c_{rs} = h_{rs}$. Then by virtue of (5·2), $h_{sr} = \bar{h}_{rs}$, and we require to discuss the solution of the system of equations

$$\Sigma_s h_{rs} q_s = \kappa q_r.$$

This depends on the determinantal equation

$$\begin{vmatrix} h_{11}-\kappa & h_{12} & \dots & h_{1n} \\ h_{21} & h_{22}-\kappa & \dots & h_{2n} \\ \cdot & \cdot & \cdot & \cdot \\ h_{n1} & h_{n2} & \dots & h_{nn}-\kappa \end{vmatrix} = 0, \quad . \quad . \quad (5{\cdot}4)$$

which we shall call the period equation.

In almost the same way as is used when the h's are real, it can be shown that this equation has only real roots *, and the same conditions hold as to the vanishing of first minors for double roots, etc. We may at once observe also that the equation only involves ω^2 ; so when ω is small compared with β, the roots will be placed symmetrically about their values for $\omega=0$—a feature of the anomalous Zeeman effect.

Associated with each root we can determine a set of ratios for the q's ; for $\kappa=\kappa_a$ we have $q_r=l_{ra}u_a$. The *normal coefficients* l_{ra} satisfy the conditions

$$\kappa_a l_{ra}=\Sigma_s l_{sa}h_{rs}. \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}5)$$

We can easily establish a set of quasi-orthogonal conditions between the normal coefficients. Thus if κ_α, κ_β are two distinct solutions of (5·4), we have

$$\Sigma_r l_{r\alpha}\tilde{l}_{r\beta}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}6)$$

As only the ratios of the l's have so far been defined, we may fix their magnitudes by the normalizing conditions

$$\Sigma_r l_{ra}\tilde{l}_{ra}=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}7)$$

When there is a double root the ratios l_{ra} are not completely determinate, but just as in the ordinary case we can always find a pair of sets of values which satisfy the orthogonal condition together. So, too, for higher degrees of multiplicity, and no trouble arises on this account. It is important to note this point because there are always multiple roots in strong magnetic fields.

When the complete system of normal coefficients has been found, we can make the substitution

$$q_r=\Sigma_a l_{ra}u_a. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}8)$$

By using (5·6) and (5·7) we can find the inverse equations, which take a form slightly different from that of the ordinary theory of vibrations about equilibrium.

$$u_a=\Sigma_r\tilde{l}_{ra}q_r. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}9)$$

We can then establish the inverted forms of the orthogonal and normalizing conditions.

$$\left.\begin{aligned}\Sigma_a l_{ra}\tilde{l}_{sa}&=0 \quad \text{if } r\neq s\\ &=1 \quad \text{if } r=s\end{aligned}\right\}, \quad . \quad . \quad . \quad (5{\cdot}10)$$

and can thence prove that

$$h_{rs}=\Sigma_a\kappa_a l_{ra}\tilde{l}_{sa}. \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}11)$$

* See, for instance, Whittaker, 'Analytic Dynamics,' p. 179.

We must also consider the behaviour of the force factors. We define

$$e_\alpha = \Sigma_r e_r \tilde{l}_{r\alpha}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}12)$$

then inverting

$$e_r = \Sigma_\alpha e_\alpha l_{r\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}13)$$

The emission function is transformed

$$\Sigma_r \tilde{e}_r q_r = \Sigma_\alpha \tilde{e}_\alpha u_\alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}14)$$

When there are equal roots, the l's are partly arbitrary. It is always possible, and often convenient, to select them in such a way that all but one of the associated force factors shall vanish.

6. *The Multiplet without Magnetic Field.*

We shall now consider the model for a multiplet without magnetic field. The system is to have all its frequencies nearly equal and their spacing is to depend on a single parameter. It would not be natural for this parameter to occur in different parts of L, and we shall therefore take it that the potential energy alone is not in the form of a sum of squares. The results would be much the same if we modified the kinetic energy instead. The atom can only be isotropic if the terms in L involving the directions x, y, z are all separated, and it will suffice to consider one of them alone. For the x-direction, we have

$$\mathrm{L} = \tfrac{1}{2}\Sigma_r(\dot{x}_r^2 - p_0^2 x_r^2) - \beta p_0 \Sigma_r \Sigma_s b_{rs} x_r x_s + \mathrm{X}\Sigma_r e_r x_r. \quad (6{\cdot}1)$$

Here X is the external electric force in the x-direction and β is small. The equations of motion are

$$\ddot{x}_r + p_0^2 x_r + 2\beta p_0 \Sigma_s b_{rs} x_s = e_r \mathrm{X}. \quad . \quad . \quad . \quad (6{\cdot}2)$$

We can solve for the natural frequencies as in (5·4) and with the help of the solution can transform (6·2) to

$$\ddot{u}_\alpha + (p_0^2 + 2p_0\kappa_\alpha)u_\alpha = e_\alpha \mathrm{X}. \quad . \quad . \quad . \quad (6{\cdot}3)$$

Under a force X proportional to e^{ipt} the emission function then is

$$\Sigma_r \tilde{e}_r x_r = \Sigma_\alpha \tilde{e}_\alpha u_\alpha = \mathrm{X}\Sigma_\alpha \frac{e_\alpha \tilde{e}_\alpha}{(p_0 + \kappa_\alpha)^2 - p^2}, \quad . \quad . \quad (6{\cdot}4)$$

and from this the refractive index can be deduced by well-known principles.

In order to discuss absorption we have to introduce damping terms into the equations. The model is illuminated by a wave of the form $\mathrm{X} = \int_0^\infty \phi(p) e^{ipt} dp$. If the damping factors are small, it is not hard to show that the response of

the model to such a force it is independent of their magnitudes; in fact, that

$$u_\alpha = -\frac{i\pi}{2} e_\alpha \frac{\phi(p_0+\kappa_\alpha)}{p_0+\kappa_\alpha} e^{i(p_0+\kappa_\alpha)t}.$$

Absorption is observed by measuring the extinction of light, initially distributed uniformly over the spectrum, as it passes through the substance. This extinction is produced by the interference between the incident light and the scattered light from the atoms. Whatever may be the mechanism of absorption inside the atoms, the external reaction must still depend on the emission function and so must give a factor $e_\alpha\tilde{e}_\alpha$ for the line of frequency $p_0+\kappa_\alpha$. The other factors are approximately constant. Thus absorption is determined from dispersion, and though we have to postulate some damping its character is without effect on the result; it only affects the breadths of the lines, a matter we are not going to discuss.

To find the emission we take arbitrary conditions of projection, so that the initial value of x_r is x_r^0 (for simplicity we omit initial velocities). Corresponding to these we can determine u_α^0, etc. by (5·9). The emission function then becomes

$$\Sigma_\alpha \tilde{e}_\alpha u_\alpha^0 e^{i(p_0+\kappa_\alpha)t},$$

and if none of the roots κ_α are equal, the intensity corresponding to the frequency $p_0+\kappa_\alpha$ is proportional to

$$|\tilde{e}_\alpha u_\alpha^0|^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\cdot5)$$

Now, if we have equipartition among the values x_r^0, we shall also have it for the u_α^0's. The average value of $u_\alpha^0|^2$ is then the same for all α, and hence the intensity of the line is proportional to $e_\alpha\tilde{e}_\alpha$. A slightly extended argument would have allowed for initial velocities. When the system contains equal roots—say κ_α, κ_β, we should get an intensity $|\tilde{e}_\alpha u_\alpha^0 + \tilde{e}_\beta u_\beta^0|^2$. This need not cause any trouble, for the choice of the normal modes is here partly undetermined, and they may be chosen so that $e_\beta=0$, and then the intensity reduces to its simpler form. We have discussed the intensities of emission and absorption for convenience without magnetic field. It is easy to see that with a few trivial changes the arguments will apply just as well when the equations of motion contain gyroscopic terms.

It is natural to choose p_0 as the centre of gravity of the multiplet. This implies a condition between the b's which we shall now work out. The centre of gravity is at p_0 if

$$\Sigma_\alpha \kappa_\alpha e_\alpha \tilde{e}_\alpha = 0.$$

Now, by (5·12), (5·11) (here simplified because all the quantities are real)

$$\Sigma_a \kappa_a e_a \tilde{e}_a = \Sigma_a \Sigma_s \Sigma_r \kappa_a e_s \tilde{l}_{sa} \tilde{e}_r l_{ra}$$
$$= \Sigma_r \Sigma_s b_{rs} e_s \tilde{e}_r = 0, \quad . \quad . \quad . \quad . \quad (6·6)$$

which is the required condition.

To illustrate the whole process we may take the following example:

$$\mathrm{L} = \tfrac{1}{2}\Sigma_1^3(\dot{x}_r^2 - p_0^2 x_r^2) + 2\beta p_0(x_1x_2 + x_2x_3 + x_3x_1) + Xex_1. \quad (6·7)$$

The period equation is

$$\begin{vmatrix} \kappa, & \beta, & \beta \\ \beta, & \kappa, & \beta \\ \beta, & \beta, & \kappa \end{vmatrix} \equiv (\kappa - \beta)^2(\kappa + 2\beta) = 0.$$

The following scheme gives the normal coefficients, etc.:

	u_1.	u_2.	u_3.
x_1	$\sqrt{2/3}$	0	$1/\sqrt{3}$
x_2	$-1/\sqrt{6}$	$1/\sqrt{2}$	$1/\sqrt{3}$
x_3	$-1/\sqrt{6}$	$-1/\sqrt{2}$	$1/\sqrt{3}$
κ_a	β	β	-2β
e_a/e	$\sqrt{2/3}$	0	$1/\sqrt{3}$

. . . (6·8)

There are thus two lines respectively at $p_0+\beta$ and $p_0-2\beta$, and the first has double the intensity of the second. In fact they are the D lines. Moreover, to conform with Minkowski's experiments e is to be given the value corresponding to that of an ordinary electron.

The form of L suggests that it might be given a more physical meaning by modifying the kinetic instead of the potential energy. In this case the complete formula for L would contain terms

$$(2\beta/p_0)(\dot{x}_1\dot{x}_2 + \dot{y}_1\dot{y}_2 + \dot{z}_1\dot{z}_2 + \dot{x}_1\dot{x}_3 + \ldots), \quad . \quad (6·9)$$

which are suggestive of electromagnetic induction. In the absence of other similar cases it is not possible to evolve this idea further.

We may here refer to an important difficulty which occurs in the designing of models. It applies to cases both with and without magnetic fields. All that is ever observed is the emission function, and it is possible for a system to have natural frequencies which never exhibit themselves. All

that is necessary for this is that the associated e_a should vanish. We shall refer to a mode of vibration having this property as *blind*, and in general the same term will be applied to any degree of freedom which has zero force factor—for example, our model for the D lines has one active and two blind electrons. The possible existence of blind vibrations makes great trouble in designing models, for their introduction often simplifies the formulæ (as an example will show below), and this compels one to try a great many more systems than would otherwise be necessary.

7. *The General Model for the Zeeman Effect.*

In the presence of a magnetic field the system is no longer isotropic, but if the field is along z there will persist a circular symmetry for x and y. As witnessed by magnetic double refraction the anisotropy is proportional to the field. We therefore construct the model by adding on gyroscopic terms; we shall take these directly proportional to the magnetic field, and shall suppose the force factors unaltered. These are the simplest assumptions we can make; we shall see later that they cannot apply to all multiplets, but nevertheless a good deal of the work can be easily adapted to such cases.

The condition of circular symmetry requires that L shall be unchanged when y is written for x and $-x$ for y, and this implies that there can be no terms in xz and yz. Consequently the terms in x and y can be separated off, and we can discuss the model for the $\perp$ components apart from the $\parallel$. As the Zeeman effect is usually described by reference to the undisplaced lines, the study of special models goes most conveniently in terms of the semi-normal form, but there is no gain in principle, so that we shall retain the generality.

We start with the most general form of L which satisfies the condition of circular symmetry.

$$\left.\begin{aligned}\mathrm{L}=\tfrac{1}{2}\Sigma_r(\dot{x}_r^2+\dot{y}_r^2-p_0^2x_r^2-p_0^2y_r^2)-\beta p_0\Sigma_r\Sigma_s b_{rs}(x_rx_s+y_ry_s)\\ +\omega\Sigma_r(x_r\dot{y}_r-\dot{x}_ry_r)+\omega\Sigma_r\Sigma_s[f_{rs}(\dot{x}_rx_s+\dot{y}_ry_s)\\ +g_{rs}(x_r\dot{y}_s-\dot{x}_sy_r)]+\mathrm{X}\Sigma e_rx_r+\mathrm{Y}\Sigma e_ry_r.\end{aligned}\right\} \quad . \quad . \quad . \quad (7{\cdot}1)$$

Here f, g are constants, and

$$f_{sr}=-f_{rs},\quad g_{sr}=g_{rs}\,; \quad . \quad . \quad . \quad . \quad (7{\cdot}2)$$

ω stands for the Larmor rotation $e\mathrm{H}/2mc$, where H is

the field, and it has been convenient to separate out a set of terms corresponding to the normal Zeeman effect.

A pair of equations is :

$$\left.\begin{aligned}\ddot{x}_r+p_0^2x_r+2\beta p_0\Sigma_s b_{rs}\dot{x}_s-2\omega\dot{y}_r+2\omega\Sigma_s(f_{rs}\dot{x}_s-g_{rs}\dot{y}_s)&=e_r\mathrm{X}.\\ \ddot{y}_r+p_0^2y_r+2\beta p_0\Sigma_s b_{rs}\dot{y}_s+2\omega\dot{x}_r+2\omega\Sigma_s(f_{rs}\dot{y}_s+g_{rs}\dot{x}_s)&=e_r\mathrm{Y}.\end{aligned}\right\} \quad . \quad . \quad . \quad (7{\cdot}3)$$

The solution can be simplified by Voigt's artifice of putting

$$\zeta_r=x_r+iy_r, \quad \mathrm{Z}=\mathrm{X}+i\mathrm{Y}. \quad . \quad . \quad . \quad (7{\cdot}4)$$

Then we have

$$\ddot{\zeta}_r+p_0^2\zeta_r+2\beta p_0\Sigma_s b_{rs}\dot{\zeta}_s+2\omega[i\dot{\zeta}_r+\Sigma_s(f_{rs}+ig_{rs})\dot{\zeta}_s]=e_r\mathrm{Z}, \quad (7{\cdot}5)$$

and a similar equation in $\bar{\zeta}_r$ and Z. To find the free vibrations we omit the right-hand side and put all co-ordinates proportional to e^{ipt}. Making a slight change in the notation, we take

$$p=p_0-\omega+\kappa. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7{\cdot}6)$$

In this way we have separated the right- and left-handed components and have referred each to the position it would have if the Zeeman effect were normal.

Write $h_{rs}=if_{rs}-g_{rs}$, then by (7·2) $h_{sr}=\bar{h}_{rs}$. . (7·7)

We omit the distinction between p and p_0 in the small terms and the equation becomes

$$-\kappa\zeta_r+\Sigma_s(\beta b_{rs}+\omega h_{rs})\zeta_s=0, \quad . \quad . \quad . \quad (7{\cdot}8)$$

and this is of the type of (5·3). In forming the corresponding equation for $\bar{\zeta}_r$ it is necessary to change the sign of ω and to take the conjugates of all the complex quantities.

The period equation is

$$\begin{vmatrix}\beta b_{11}+\omega h_{11}-\kappa, & \beta b_{12}+\omega h_{12}, & \ldots\\ \beta b_{21}+\omega h_{21}, & \beta b_{22}+\omega h_{22}-\kappa, & \ldots\\ \ldots & \ldots & \ldots\end{vmatrix}=0, \quad (7{\cdot}9)$$

and according to the relative magnitudes of β and ω we have the anomalous Zeeman effect and the Paschen-Back effect. We shall refer to these simply as the *weak* and *strong effects* respectively. To deal with the weak effect we refer the system to its vibrations without field, that is we suppose L reduced to its semi-normal form, and this is given if we take $b_{rs}=0$ for $r\neq s$. The period equation will then separate into groups for each of which b_{rr}'s have the same value. For example, if one member of the multiplet shows a

Zeeman effect with two components, we must have $b_{11}=b_{22}$, and can then separate out from (7·9) an equation

$$\begin{vmatrix} \beta b_{11}+\omega h_{11}-\kappa, & \omega h_{12} \\ \omega h_{21}, & \beta b_{11}+\omega h_{22}-\kappa \end{vmatrix} =0. \quad (7\cdot10)$$

The known positions of the components then give us two relations between h_{11}, h_{12}, h_{21}, h_{22}.

Now consider the strong effect, where all multiplets give the normal Zeeman effect. To examine it we simply omit the terms in β. Now it is obviously not possible for all the roots of (7·9) to vanish, for this would imply a normal effect also in weak fields; but this is not needed, it is enough if all solutions are blind for which $\kappa\neq0$. The necessary and sufficient condition for the strong effect is thus that for any κ_a differing from zero the emission function should vanish, that is, $\Sigma_r \bar{e}_r l_{ra}=0$. This implies that the set of quantities e_r are orthogonal to the normal coefficients l_{ra} which belong to every non-zero root κ_a. Hence, as the e_r's cannot all vanish, they must be a set of normal coefficients for one of the modes orthogonal to all these, that is, for some mode for which $\kappa=0$. Substituting in (5·5) we thus get

$$\Sigma_s e_s h_{rs}=0, \quad . \quad . \quad . \quad . \quad . \quad (7\cdot11)$$

and as it is easy to see that these conditions imply that at least one root of the period equation must vanish, they constitute a set of necessary and sufficient conditions for the strong effect.

In one particular case the strong condition can be given an even simpler form. Suppose, as in the example of the last section, that only one electron is active and all the rest are blind. Then we have $e_r=0$ except for e_1. The conditions for the strong effect then are simply that $h_{r1}=0$ for all r.

By the general argument of § 5 the II components will be symmetrical about the undisplaced lines in weak fields. L will only involve z's, and there will be a set of gyroscopic terms with coefficients proportional to ω. We take $\kappa=p_0-p$ in this case and the argument goes much as before; the only distinction is that the system of equations does not split into two, and that the h's are purely imaginary. The condition for the strong effect is exactly as before.

8. *The Magnetic Gyration of Light.*

The assumed form of model implies an interesting theorem concerning the Faraday effect. However weak the field, light of wave-length distant from the multiplet will show no

trace of the anomalous effect, but will be rotated to an extent exactly given by the normal Zeeman effect. There is a crude way of explaining magnetic gyration which leads to a wrong result. The argument is as follows. Draw a complete dispersion curve for the undisplaced line, and copy it twice displaced respectively to the right and left. As one wave corresponds to right-handed polarized light and the other to left-handed, the difference between the two curves should give the net rotatory effect. If the line splits into more than a single pair of components we should expect that an appropriate averaging of their influences would give the right result. This argument would suggest for the rotation of sodium an amount equal to

$$(1\times\tfrac{5}{3}+3\times 1+2\times\tfrac{4}{3})/(1+3+2)=11/9$$

of the normal rotation. The fallacy lies in the assumption that the dispersion curves may be shifted unchanged in form. This is only approximately true ; the comparative importance of the various lines changes only slightly with the field, but as the gyration is itself a differential effect, these small changes become sensible.

Let the amplitude of the incident light be proportional to e^{ipt}, and now suppose that p is not at all near to p_0. The equations of motion are

$$\zeta_r(p_0^2-p^2-2\omega p)+2\beta p_0\Sigma_s b_{rs}\zeta_s+2\omega p\Sigma_s h_{rs}\zeta_s=e_r Z. \quad (8{\cdot}1)$$

The first term is now large, and we can solve by approximation and have

$$\zeta_r=Z\left\{\frac{e_r}{p_0^2-p^2}-2\beta p_0\Sigma_s\frac{b_{rs}e_s}{(p_0^2-p^2)^2}+2\omega p\frac{e_r}{(p_0^2-p^2)^2}\right.$$
$$\left.-2\omega p\Sigma_s\frac{h_{rs}e_s}{(p_0^2-p^2)^2}\right\}. \quad . \quad . \quad . \quad (8{\cdot}2)$$

Then the emission function is

$$\Sigma_r\tilde{e}_r\zeta_r=Z\left\{\Sigma_r\frac{e_r\tilde{e}_r}{p_0^2-p^2}-2\beta p_0\Sigma_r\Sigma_s\frac{b_{rs}e_s\tilde{e}_r}{(p_0^2-p^2)^2}\right.$$
$$\left.+2\omega p\Sigma\frac{e_r\tilde{e}_r}{(p_0^2-p^2)^2}-2\omega p\Sigma_r\Sigma_s\frac{h_{rs}e_s\tilde{e}_r}{(p_0^2-p^2)^2}\right\}. \quad (8{\cdot}3)$$

By (6·6) the second term will vanish if p_0 has been chosen as the centre of gravity of the multiplet. The fourth vanishes by virtue of (7·11), the conditions for the strong effect. Consequently

$$\Sigma_r\tilde{e}_r\zeta_r=Z\Sigma_r\frac{e_r\tilde{e}_r}{p_0^2-p^2}\left(1+\frac{2\omega p}{p_0^2-p^2}\right), \quad . \quad . \quad (8{\cdot}4)$$

which is exactly the result that would be obtained if there

were no anomalous Zeeman effect at all. So we conclude that light at any considerable distance from the multiplet will be gyrated according to the normal Lorentz principle, no matter how weak the magnetic field. When the incident light has frequency near that of the multiplet of course this does not hold, since the approximate method of solution fails; here the actual anomalies of the Zeeman effect will show themselves. In intermediate cases formulæ can be found by regarding ω, but no longer β, as small compared to $p-p_0$. The validity of Voigt's type of model could evidently be partially tested by experiments which verified whether the dispersion becomes normal at great distances from the multiplet.

There is a well-known formula, due to Becquerel *, whereby the value of e/m for any substance can be deduced from measures of its gyration and dispersion, and these measures need not be carried out near its regions of absorption. The formula is

$$\mathrm{R}=\frac{e}{2mc^2}\lambda\frac{dn}{d\lambda}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8{\cdot}5)$$

where

n is the refractive index,
λ is the wave-length,
R is the "Verdet constant,"
and e is measured in E.S.U.

This has been applied to a good many substances, and with one exception the values found are well below the normal value. The anomalous Zeeman effect always involves increased values of e/m, and our theorem shows that we need not expect these to be reproduced in Becquerel's formula. There remains the difficulty of the values being too low. The infra-red bands of a substance depend on nuclear motions and so should lower the value, but they play quite an insignificant part in the refraction of blue and ultra-violet light. We should thus expect that if e/m is calculated from (8·5) for different wave-lengths, the values will be low in the infra-red and increase towards a limit in the ultra-violet. Tho following figures show this for the case of water, which has a band in the near infra-red.

Wave-length in μ	1·000	·900	·800	·701	·589	·518	·437	·361	·275	·250
$\frac{e/m}{(e/m)_{\text{norm.}}}\times 100$	26	33·6	47·5	59·6	68·0	74·2	77·4	78·3	78·6	78·7

More striking is the case of the permanent gases, since they

* Becquerel, *C. R.* vol. cxxv. p. 679 (1897).

have no infra-red absorption. Thus hydrogen gives a value within 1 per cent. of the normal for all wave-lengths not very near to the point in the far ultra-violet where it ceases to be transparent—this is the only substance known that is normal; whereas nitrogen gives 69 per cent. normal over the same range of wave-lengths. The fact that it is hydrogen that is normal shows that the abnormality cannot be due to nuclear motions, for these would certainly be larger in hydrogen than in anything else. On the lines of the present section we can only get the observed result by supposing that the absorption bands in the ultra-violet show an anomalous Paschen-Back effect! An alternative and more probable explanation will be given in the next section.

9. *The Failure of the Model for some Lines.*

Consideration of a certain type of multiplets shows that the model with which we have been working cannot always be adequate. Take the line 2537 of mercury. This is the only surviving member of a triplet $1S–2p$. In a magnetic field it gives a single pair of $\perp$ components, but with a separation 3/2 of the normal. This could, of course, be easily represented mechanically, but would of necessity imply the same abnormality in strong fields. In order to represent the strong effect we must bring in the other lines of the triplet somehow. Now a triplet would only show two lines if the force factor associated with the third happened to vanish in the absence of the field. In this case it would be observed that the absent line began to make its appearance with an intensity proportional to the square of the magnetic force, and the strong effect could finally appear in the normal way. Unfortunately this explanation will not do if only one line of the triplet is ordinarily present. For let us suppose that the model is reduced to semi-normal form, and that it is the line 1 that is active. All the force factors except e_1 vanish, even if 1 is a multiple root. The condition for the strong effect is then that $h_{r1}=0$ and in particular that $h_{11}=0$, and so there can be no anomalous weak effect.

The only way of overcoming this difficulty seems to be to alter our assumptions and to suppose that the h's and e's are themselves functions of the magnetic field. The conditions for the strong effect will take exactly the same form as before, but owing to the variability of the parameters will not be nearly so significant. In the strong field (7·11) will still be true, but we shall not be able to apply it to (8·3),

because the e's and h's will there have different values. The transition from the weak to the strong effect in mercury can be made to occur either by varying the e's or the h's; it should be accompanied by the appearance of the other lines of the triplet with intensities proportional to the square of the field. When the field is weak we need no longer have $\Sigma_s e_s h_{rs}=0$, and so there is no longer any necessity that Becquerel's formula should lead to the normal e/m.

A piece of evidence in favour of making the h's vary is provided by the theory of Landé referred to in § 3. This suggests that Voigt's values of the Zeeman effect for intermediate fields are wrong, and the only way of altering them is to allow the h's to change. The conditions for the strong effect are not at all stringent and can be satisfied by a very wide choice of e's and h's.

The importance of this part of our work lies in the fact that gyration gives information about the beginnings of the transition from the weak to the strong effect. It does not show how the positions of the components change, but partially reveals the change in their relative intensities to a higher order than is directly observable. The quantum theory has successfully explained the intensities in weak fields, and the suggested information should act as a help to its further development. The experiment has the advantage of only depending on refinements in optics, whereas most methods of attack would seem to involve the production of magnetic fields of such great strength as must always be unattainable.

10. *The* D *Lines*, ⊥ *Component.*

With the use of the principles of §§ 5–7 we shall now discuss the complete model for the doublet. For the ⊥ components Sommerfeld gives the equations

$$\left.\begin{aligned}
&\ddot{\zeta}_1+2i\omega\dot{\zeta}_1+p_1{}^2\zeta_1+\tfrac{2}{3}i\omega(\dot{\zeta}_1+\epsilon\dot{\zeta}_2+\epsilon^2\dot{\zeta}_3)=eZ,\\
&\ddot{\zeta}_2+2i\omega\dot{\zeta}_2+p_2{}^2\zeta_2+\tfrac{2}{3}i\omega(\dot{\zeta}_2+\epsilon\dot{\zeta}_3+\epsilon^2\dot{\zeta}_1)=eZ,\\
&\ddot{\zeta}_3+2i\omega\dot{\zeta}_3+p_2{}^2\zeta_3+\tfrac{2}{3}i\omega(\dot{\zeta}_3+\epsilon\dot{\zeta}_1+\epsilon^2\dot{\zeta}_2)=eZ,
\end{aligned}\right\}. \quad (10{\cdot}1)$$

where p_1, p_2 are the frequencies of D_1 and D_2 and ϵ is a cube root of unity. These equations, of course, represent a mechanical system, but if we put down the Lagrangian from which they are derived it will be found to contain a very

large number of terms, some of which involve the irrationality $\sqrt{3}$ arising from ϵ. In fact, in spite of the symmetry, the model is not really simple. Another point in which it cannot be supposed to be very near to reality is that it requires three similar electrons, and the quantum theory leads us to expect that in sodium one electron is more important than all the others. This matter was discussed in § 3 and need not be further dealt with here.

We have shown how the doublet can be simplified by departing from the semi-normal form, when there is no field. If we take that idea and transform Voigt's equations by means of it we arrive (by rather heavy algebra involving the special choice of one parameter) at a new form from which all irrationalities have disappeared. As we are going to discuss the making of models later, we shall simply here give the result. Take

$$\left.\begin{aligned} \mathrm{L} = {} & \tfrac{1}{2}\Sigma_1{}^3(\dot{x}_r{}^2+\dot{y}_r{}^2)-\tfrac{1}{2}p_0{}^2\Sigma_1{}^3(x_{r1}{}^2+y_r{}^2) \\ & +2\beta p_0(x_1x_2+y_1y_2+x_2x_3+y_2y_3+x_1x_3+y_1y_3) \\ & +\omega(x_1\dot{y}_1-\dot{x}_1y_1)+\tfrac{1}{2}\omega(x_2\dot{y}_2-\dot{x}_2y_2+x_3\dot{y}_3-\dot{x}_3y_3) \\ & +\tfrac{1}{2}\omega(x_2\dot{x}_3-\dot{x}_2x_3+y_2\dot{y}_3-\dot{y}_2y_3)+e(\mathrm{X}x_1+\mathrm{Y}y_1) \end{aligned}\right\}. \quad (10{\cdot}2)$$

The equations of motion in x and y can be combined into equations in ζ as in § 7. These are

$$\left.\begin{aligned} & \ddot{\zeta}_1+p_0{}^2\zeta_1-2\beta p_0(\zeta_2+\zeta_3)+2i\omega\dot{\zeta}_1=e\mathrm{Z}, \\ & \ddot{\zeta}_2+p_0{}^2\zeta_2-2\beta p_0(\zeta_3+\zeta_1)+3i\omega\dot{\zeta}_2-\omega\dot{\zeta}_3=0, \\ & \ddot{\zeta}_3+p_0{}^2\zeta_3-2\beta p_0(\zeta_1+\zeta_2)+3i\omega\dot{\zeta}_3+\omega\dot{\zeta}_2=0. \end{aligned}\right\}. \quad (10{\cdot}3)$$

The strong effect is verified at once because the coefficient of $\dot{\zeta}_1$ is simply $2i\omega$. We shall not examine the complete solution for all strengths of field, because the equations are only transformations of those of Voigt, and so must give exactly the same frequencies and intensities. But as illustrating the type of solution we shall give the weak effect. The period equation is (with $p=p_0-\omega+\kappa$)

$$\begin{vmatrix} \kappa, & \beta, & \beta \\ \beta, & \kappa+\frac{\omega}{2}, & \beta+\frac{i\omega}{2} \\ \beta, & \beta-\frac{i\omega}{2}, & \kappa-\frac{\omega}{2} \end{vmatrix} \equiv(\kappa-\beta)[(\kappa+\omega)(\kappa+\beta)-2\beta^2]=0. \quad . \quad . \quad . \quad (10{\cdot}4)$$

The approximate solutions are $\kappa=\beta,\ \beta-\frac{2}{3}\omega,\ -2\beta-\frac{1}{3}\omega$, and the complete determination of the frequencies and normal coefficients is given in the following scheme :—

	u_1.	u_2.	u_3.
ζ_1	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
ζ_2	$\frac{-1+i}{2\sqrt{2}}$	$\frac{-1-3i}{2\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
ζ_3	$\frac{-1-i}{2\sqrt{2}}$	$\frac{-1+3i}{2\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$p-p_0$	$\beta-\omega$	$\beta-\frac{5}{3}\omega$	$-2\beta-\frac{4}{3}\omega$
e_a/e	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$

. . (10·5)

It must be remembered that this is to be read horizontally, thus

$$\zeta_2=\frac{-1+i}{2\sqrt{2}}u_1+\frac{-1-3i}{2\sqrt{6}}u_2+\frac{1}{\sqrt{3}}u_3.$$

If it is wished to read it vertically the conjugates must be taken, thus:

$$u_1=\frac{1}{\sqrt{2}}\zeta_1+\frac{-1-i}{2\sqrt{2}}\zeta_2+\frac{-1+i}{2\sqrt{2}}\zeta_3.$$

From the force factors we at once derive that the intensities of the lines are as $\frac{1}{2}:\frac{1}{6}:\frac{1}{3}$ or $3:1:2$, as is confirmed by experiment. This is subject to the assumption of equipartition between the coordinates, and if we imagined special forms of excitation, we could obtain other results. For example, suppose that the second electron was alone excited. From (6·5) we should then have intensities in the ratios $(\frac{1}{4}\cdot\frac{1}{2}):(\frac{10}{24}\cdot\frac{1}{6}):(\frac{1}{3}\cdot\frac{1}{3})$ or $18:10:16$. If only the first were excited they would be $9:1:4$. Resonance radiation must be supposed to arise from action on the first electron, and the erroneous values for the intensities are a further proof of the necessity for some sort of reorganization between the processes of absorption and re-emission.

11. *The* D *Lines,* ∥ *Component.*

Voigt's model for the ∥ components is a little more artificial, for he introduces two frequencies which are blind at all strengths of the field. By this means he splits the equations of motion into half in the same way as can always be done for the ⊥ components. His equations are

$$\left.\begin{aligned}
&\ddot{\zeta}_1+2i\omega\dot{\zeta}_1+p_1^2\zeta_1-\tfrac{2}{3}i\omega(\dot{\zeta}_1+\dot{\zeta}_2+\dot{\zeta}_3)=eZ',\\
&\ddot{\zeta}_2+2i\omega\dot{\zeta}_2+p_2^2\zeta_2-\tfrac{2}{3}i\omega(\dot{\zeta}_1+\dot{\zeta}_2+\dot{\zeta}_3)=eZ',\\
&\ddot{\zeta}_3+2i\omega\dot{\zeta}_3+p_2^2\zeta_3-\tfrac{2}{3}i\omega(\dot{\zeta}_1+\dot{\zeta}_2+\dot{\zeta}_3)=eZ',
\end{aligned}\right\}. \quad (11{\cdot}1)$$

where $\zeta=z+iw$, $Z'=Z(1+i)$.

The extra coordinates w make the completed system anisotropic unless the force factors are chosen to be $1/\sqrt{2}$ of the corresponding ones for the ⊥ coordinates. If we apply the transformation quoted in the last section to these equations, we obtain

$$\left.\begin{aligned}
L=\tfrac{1}{2}\Sigma_1^3[&(\dot{z}_r^2+\dot{w}_r^2)-p_0^2(z_r^2+w_r^2)]\\
&+2\beta p_0(z_1z_2+z_2z_3+z_3z_1+w_1w_2+w_2w_3+w_3w_1)\\
&+\omega(z_2\dot{w}_2-\dot{z}_2w_2+z_3\dot{w}_3-\dot{z}_3w_3)+Zez_1.
\end{aligned}\right\}. \quad (11{\cdot}2)$$

We have made a small further change in that Z is the actual electric force, so that w_1 is blind, and we have avoided the necessity of having a force factor different from those of x_1 and y_1. The strong condition is satisfied by the absence of terms in ω involving z_1.

As before, we shall only give the effects in weak fields; in stronger fields they go exactly as in Sommerfeld's paper *. We follow him in splitting the equations into two by the substitution $\zeta=z+iw$ and have equations

$$\left.\begin{aligned}
&\ddot{\zeta}_1+p_0^2\zeta_1-2\beta p_0(\zeta_2+\zeta_3)=eZ,\\
&\ddot{\zeta}_2+p_0^2\zeta_2-2\beta p_0(\zeta_1+\zeta_3)+2i\omega\dot{\zeta}_2=0,\\
&\ddot{\zeta}_3+p_0^2\zeta_3-2\beta p_0(\zeta_1+\zeta_2)+2i\omega\dot{\zeta}_3=0.
\end{aligned}\right\}. \quad . \quad (11{\cdot}3)$$

Taking $p=p_0+\kappa$, the period equation is

$$\left|\begin{matrix}\kappa, & \beta, & \beta\\ \beta, & \kappa+\omega, & \beta\\ \beta, & \beta, & \kappa+\omega\end{matrix}\right|\equiv(\kappa-\beta+\omega)[(\kappa-\beta)(\kappa+2\beta)+\kappa\omega]=0, \quad . \quad . \quad . \quad (11{\cdot}4)$$

* Sommerfeld, *loc. cit.*

and the normal coefficients are given by the scheme

	u_1.	u_2.	u_3.
ζ_1	0	$\frac{2}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
ζ_2	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
ζ_3	$-\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$
$p-p_0$	$\beta-\omega$	$\beta-\frac{1}{3}\omega$	$-2\beta-\frac{2}{3}\omega$
e_α/e	0	$\frac{2}{\sqrt{6}}$	$\frac{1}{\sqrt{3}}$

. . (11·5)

The intensities are in the ratio 0 : 2 : 1.

Before leaving the subject of models for doublets, we may note that in both ⊥ and ∥ components the coordinates x_1, y_1, z_1 alone have force factors, so that we may, so to speak, regard the rest as having no sense of direction. This suggests that the blind coordinates called x_2 etc. might really be in some quite other direction, and if they were we could in some ways give the formulæ more natural interpretations. Thus we might regard the coefficient of ω in (11·2) as due to the fact that z_2, z_3 were really in the direction x, and w_2, w_3 in the direction y, and then we could interpret these terms as a normal effect of the magnetic field. The main difficulty is that, in proportion as we give these terms simple meanings, the terms in the potential energy become complicated. Without some model for another type of multiplet to guide us we cannot see which of several forms is the most natural, and so shall leave our model as it stands.

12. *The Construction of Models.*

We now consider what general principles ought to guide us in designing models for other types of multiplet. These have, of course, to conform to specified conditions as to frequencies and intensities. This means that we are given a set of u's and their force factors, and our object is to discover a linear transformation which will reduce them to equations derived from some simple Lagrangian function. We are to preserve the condition that the kinetic energy remains a sum

of squares, and so the permissible transformations are any set of mutually orthogonal coefficients. Now even when we restrict them to being real quantities, this gives a quite impracticably large field of choice—for three degrees there are three arbitrary parameters, for four there are six and so on, and when the coefficients may be complex the number is still larger. So there is no hope in applying the general transformation and at the end selecting particular simplifying values. Under these conditions we naturally take the doublet as guide and try to find a special transformation which will have the same features. In the first place we have to arrange for the lines without field. This we should attempt by a modification of the potential energy only, and the x direction can be treated alone. The first difficulty is to choose the number of variables, because there does not appear to be any simple way of expanding the number during the work. As a lower limit we can take the number of Zeeman components, but it is always possible (as happens in the II component of a doublet) that the introduction of blind vibrations would simplify the expressions. To have a satisfactory system the one parameter which determines the intervals of the multiplet must occur in L multiplying an expression which only involves simple arithmetical coefficients. The semi-normal form would fulfil this condition, but not well, as it would fail to link together the different variables, and would have just the same form even if the separate intervals were not related. If, further, we introduce the principle that there shall be only one active electron it is definitely ruled out, since the semi-normal form requires a force factor for each line proportional to the square root of its intensity.

I have tried two methods of discovering models which obey these rules. The first is to make up determinants having certain rows so arranged that by subtraction a factor could be taken out, the constants being adjusted so that all the roots come right. Even if this could be done there would remain the probability that the force factors would not correspond to one single active electron; but, as a matter of fact, I have not succeeded in finding any determinant of this type for either a $1s$–mp triplet or a $2p$–md doublet*. All attempts seem to require the determinant to have some root much further from the rest than is given by any of the lines, so that to use the method there would have to be some

* In this case there would be two parameters, corresponding to the separations of the p and d terms respectively.

rather elaborate condition so as to blind this root. The second method has the advantage of certainly producing an answer of some kind. This is to construct a complete set of mutually orthogonal coefficients, selecting them as far as possible to avoid anything but simple numbers. The difficulty in this method is that the coefficients always must involve square roots, and that while they are being constructed it is very hard to see which will lead to the simplification of the coefficients in the potential energy. We shall give later an example of this process, so that it need not be further elaborated here.

To form a model for the Zeeman effect it is best to start with the semi-normal form. Then for each line of the multiplet there will be a set of relations for the h's and further relations for the e's. These may be insufficient to determine them completely and we choose the simplest conditions that can be found. When these are fixed we must put in the strong conditions, which give equations limiting the values of the h's interrelating different members of the multiplet. There will not usually be enough relations to fix them completely and we must guess the rest to help the simplification. A knowledge of the frequencies in intermediate fields would decide some of these arbitrary values. When all the coefficients have been determined we have lastly to transform the whole to the form in which the potential energy is modified.

We shall illustrate the procedure by two examples. The first gives a model for the ∥ components of a doublet without the blind solutions of Voigt. The second gives the whole process for the ⊥ components of a normal triplet.

13. *An Alternative Model for the* ∥ *Components of the* D *Lines.*

The D lines have in all four ∥ components, and so we must have at least four variables to represent them. We therefore take a form in z like (6·7), and add on to it terms in z_4 which give the frequency of D_1 when there is no field. We make z_4 blind so that the intensities will be unaffected. To this expression we then add on the general form for the gyroscopic terms. Then L is

$$\left.\begin{aligned} &\tfrac{1}{2}\Sigma_1{}^4(\dot{z}_r{}^2-p_0{}^2z_r{}^2)+2\beta p_0(z_1z_2+z_1z_3+z_2z_3+2z_4{}^2)\\ &\quad+Zez_1+\omega\Sigma_r\Sigma_s c_{rs}\dot{z}_rz_s \quad (c_{sr}=-c_{rs}). \end{aligned}\right\} . \quad (13\cdot1)$$

The strong condition at once requires that c_{1r} should vanish

for all r. We next have to fit in the weak effect. The period equation for $p=p_0+\kappa$ is

$$\begin{vmatrix} \kappa, & \beta, & \beta, & 0 \\ \beta, & \kappa, & \beta-i\omega c_{23}, & -i\omega c_{24} \\ \beta, & \beta+i\omega c_{23}, & \kappa, & -i\omega c_{34} \\ 0, & i\omega c_{24}, & i\omega c_{34}, & \kappa+2\beta \end{vmatrix} =0. \quad (13{\cdot}2)$$

The determinant only involves ω^2, so the roots will be symmetrical about D_1 and D_2. We are to have a root at $p=p_0+\beta+\frac{1}{3}\omega$. Substitute this value and make the determinant vanish to the first order in ω. This requires that $c_{23}^2=\frac{1}{3}$. Next put $p=p_0-2\beta+\frac{2}{3}\omega$, and in the same way we find that the determinant only vanishes if $(c_{24}+c_{34})^2=\frac{4}{3}$. All conditions as to frequency are satisfied, but in view of the symmetry in the coordinates z_2 and z_3, we naturally take $c_{24}=c_{34}$. Thus we have $c_{23}=c_{24}=c_{34}=\dfrac{1}{\sqrt{3}}$ (the ambiguity of sign is unimportant as it depends on arbitrary signs of the variables z_2, z_3, z_4). Thus the gyroscopic terms are

$$\frac{\omega}{\sqrt{3}}(\dot{z}_2z_3-z_2\dot{z}_3+\dot{z}_2z_4-z_2\dot{z}_4+\dot{z}_3z_4+z_3\dot{z}_4). \quad (13{\cdot}3)$$

The intensities are of course correct, since in the weak field they are dictated simply by the values for no field. As a matter of fact, analysis shows that for all strengths of field the frequencies and intensities are exactly the same as those given by Voigt's model.

This model raises two points of interest. In the first place we have made the arbitrary choice that $c_{24}=c_{34}$. If we take other values subject to $c_{24}+c_{34}=\dfrac{2}{\sqrt{3}}$ we obtain as period equation

$$(\kappa-\beta)^2(\kappa+2\beta)^2=\omega^2[\kappa^2+\theta(\kappa-\beta)(\kappa+2\beta)]$$

where θ is arbitrary. Only if $\theta=0$ can this be split into two quadratics, except in the limit when ω is small. So the general form will involve as frequencies the roots of an irreducible quartic. If Landé's formulæ for intermediate fields are right it might be possible to get a model giving a closer approximation by a suitable choice of θ; but as there is only one adjustable parameter, it seems most unlikely that the improvement would extend very far. The other point to observe is that the irrationality $\sqrt{3}$ which we got rid of in our transformation of the $\perp$ model has reappeared again.

This suggests that in other cases as well the introduction of blind roots may be able to reduce complicated expressions to much simpler forms. As there is nothing to tell us what values are to be taken for these blind roots, this fact is not very helpful in the actual designing of models.

14. *The Triplet without Field.*

We now consider the design of a model for a triplet. The first task is to find the model for the undisplaced lines. These have separations in the ratio 1 : 2, and intensities in the ratios 1 : 3 : 5. Referring them to the centre of gravity, we thus have roots at $p_0-2\beta$ with a force factor $\frac{e}{3}$, others at $p_0-\beta$ with factor $\frac{e}{\sqrt{3}}$, and others at $p_0+\beta$ with $\frac{\sqrt{5}e}{3}$ *.

The Zeeman effect prescribes six as the minimum number of degrees of freedom, one for the first root, two for the second, and three for the third. We shall only use this number, but may note that there is some indication that nine would be better. One reason is that the sum of the intensities adds up to 9, just as in the doublet the sum of the intensities adds up to 3, and another reason will be given below. The calculation for 9 degrees with 3 vibrations blind is, however, too impossibly heavy to pursue.

We therefore proceed to construct an orthogonal set of real coefficients of six rows, which must obey the following conditions. The period equation is to reduce to

$$(\kappa+2\beta)(\kappa+\beta)^2(\kappa-\beta)^3=0.$$

The force factors in the normal form are to be

$$\frac{1}{3},\ \frac{1}{\sqrt{3}},\ 0,\ \frac{\sqrt{5}}{3},\ 0,\ 0.$$

There is no loss of generality in taking three of them zero in this way, and it will have no effect on the algebraic form of L from which the motion is derived. These conditions are absolute. In addition we have to try as far as possible to build a form like that of the doublet. In the first place we take only one electron active and make the five others blind. This at once determines the first row of the orthogonal coefficients by (5·12) and therefrom the coefficient b_{11} (substituting b for h in (5·11)). We next have to compose the second row of coefficients. Here the choice is very wide,

* In the absence of experimental evidence we are assuming that only one electron is active. This fits in best with the quantum theory, but there remains the possibility that both valence electrons should be active.

so we take as many of them zero as possible. The values adopted are then used to calculate b_{12} and b_{22}. Trials are made until values are found which make them simple in form. A particular guide which I used in selecting the coefficients was that the coefficients of the square terms b_{rr} should vanish, as they do in the doublet. The argument for this is not very cogent, but it seems natural to regard the coefficient of a square term as really going with the main term in p_0^2 and so describing a period different from the rest, and there seems no reason that such a new period should have a simple arithmetical relation to the coefficients of product terms. Unfortunately it is not possible to be consistent in this last rule, for with six degrees we can see that at least one square coefficient cannot vanish. By (5·11)

$$\begin{aligned}\Sigma_r b_{rr} &= \Sigma_r \Sigma_a \kappa_a l_{ra} l_{ra} \\ &= \Sigma_a \kappa_a = -\beta.\end{aligned}$$

It is this fact that suggested the appropriateness of using nine degrees of freedom, for in that case all the square coefficients can vanish. However, even though we do not get a theoretical justification for the choice, it is still most useful in helping to decide between a great number of otherwise perfectly indifferent choices. Proceeding on these lines I have constructed orthogonal systems of which the following is perhaps the simplest:

	u_1.	u_2.	u_3.	u_4.	u_5.	u_6.
x_1	1/3	$1/\sqrt{3}$	0	$\sqrt{5}/3$	0	0
x_2	0	0	$1/\sqrt{2}$	0	$1/\sqrt{2}$	0
x_3	0	0	$1/\sqrt{2}$	0	$-1/\sqrt{2}$	0
x_4	1/3	$1/\sqrt{3}$	0	$-4/3\sqrt{5}$	0	$1/\sqrt{5}$
x_5	$-1/\sqrt{3}$	0	0	$1/\sqrt{15}$	0	$3/\sqrt{15}$
x_6	2/3	$-1/\sqrt{3}$	0	$1/3\sqrt{5}$	0	$1/\sqrt{5}$
$p-p_0$	-2β	$-\beta$	$-\beta$	β	β	β

(14·1)

From these we construct the potential energy by means of (5·11).

Finally the Lagrangian function is

$$\begin{aligned}&\tfrac{1}{2}\Sigma_1^6(\dot{x}_r^2 - p_0^2 x_r^2) - \tfrac{1}{2}\beta p_0\big[-x_2x_3 - x_1x_4 \\ &\quad + \frac{1}{\sqrt{3}}(x_1 + x_4 + 2x_6)x_5 - \tfrac{1}{2}x_6^2\big] + e\mathrm{X}x_1, \quad (14·2)\end{aligned}$$

and this will give rise to the triplet with correct intervals and intensities. One or two other forms were also constructed, but none was free from irrationalities. There is no claim that the form represents any sort of physical reality, but for the sake of illustration we shall use it in dealing with the Zeeman effect.

15. *The Zeeman Effect of the Triplet.*

The frequencies of the components of the Zeeman effect have long been known, and recently the intensities have been conclusively fixed by theoretical principles *, though apparently they have not been verified experimentally. We are only going to treat of the ⊥ components and these are given in the following scheme :—

Frequency	$-2\beta\pm2\omega$	$-\beta\pm\frac{3}{2}\omega$	$-\beta\pm2\omega$	$\beta\pm\omega$	$\beta\pm\frac{3}{2}\omega$	$\beta\pm2\omega$
Intensity	1	$\frac{3}{2}$	$\frac{3}{2}$	3	$\frac{3}{2}$	$\frac{1}{2}$

These are, of course, the weak effect, and to find the model we shall start with the semi-normal form, and use equations like (7·8) involving $x+iy=\zeta$. The equations of motion then fall into three groups, the first in ζ_1, the second in ζ_2, ζ_3, and the third in ζ_4, ζ_5, ζ_6. From the weak effect we determine relations for the h's within each group. Also as we have already worked out an orthogonal system which we intend to use subsequently, we lay down that our ζ's are to have force factors $\frac{1}{3}$, $\frac{1}{\sqrt{3}}$, 0, $\frac{\sqrt{5}}{3}$, 0, 0.

The motion of ζ_1 must then be †

$$\ddot{\zeta}_1+(p_0-2\beta)^2\zeta_1-2i\omega(1+h_{11})\dot{\zeta}_1=\tfrac{1}{3}e\mathrm{Z}, \quad . \quad (15\cdot1)$$

or if $p=p_0+\omega+\kappa$ and ζ_1, Z vary as e^{ipt},

$$2p_0\zeta_1(-\kappa-2\beta+\omega h_{11})=\tfrac{1}{3}e\mathrm{Z}.$$

The period equation is to be

$$\kappa=-2\beta+\omega \text{ and so } h_{11}=1. \quad . \quad . \quad . \quad (15\cdot2)$$

The intensity is, of course, correct for a line standing alone like this.

The motion of ζ_2, ζ_3 is given by

$$\left.\begin{aligned}\ddot{\zeta}_2+(p_0-\beta)^2\zeta_2-2i\omega[1+h_{22})\dot{\zeta}_2+h_{23}\dot{\zeta}_3]&=\frac{1}{\sqrt{3}}e\mathrm{Z},\\ \ddot{\zeta}_3+(p_0-\beta)^2\zeta_3-2i\omega[h_{32}\dot{\zeta}_2+(1+h_{33})\dot{\zeta}_3]&=0.\end{aligned}\right\}. \quad (15\cdot3)$$

* Ornstein & Burger, *Z. f. P.* xxviii. p. 135 (1925).

† The signs of ω and the h's happened to be changed in this work, but it appeared unnecessary to alter them into conformity with § 7.

In the same way these reduce to

$$\left.\begin{aligned} 2p_0\zeta_2(-\kappa-\beta+\omega h_{22})+2p_0\zeta_3\omega h_{23}&=\frac{1}{\sqrt{3}}eZ,\\ 2p_0\zeta_3\omega h_{32}+2p_0\zeta_3(-\kappa-\beta+\omega h_{33})&=0. \end{aligned}\right\} \quad (15{\cdot}4)$$

The period equation is

$$\begin{vmatrix} -\kappa-\beta+\omega h_{22}, & \omega h_{23} \\ \omega h_{32}, & -\kappa-\beta+\omega h_{33} \end{vmatrix}=0,$$

and this is to have roots $\kappa+\beta=\frac{1}{2}\omega$, ω with equal intensities. Thus $h_{22}+h_{33}=\frac{3}{2}$ and $h_{22}h_{33}-h_{23}h_{32}=\frac{1}{2}$. To determine the intensities we find the normal coefficients for each frequency, and get

$$\zeta_2=-\sqrt{2h_{33}-1}\,u_2+\sqrt{2-2h_{33}}\,u_3,$$

and an expression for ζ_3 which we do not require. For equal intensities the coefficients of u_2 and u_3 must be equal. Hence $h_{33}=\frac{3}{4}$, and so $h_{22}=\frac{3}{4}$ and $|h_{23}|=\frac{1}{16}$. There seems to be nothing gained by taking h_{23} complex, and so we have $h_{23}=\frac{1}{4}$.

The coefficients for ζ_4, ζ_5, ζ_6 are more troublesome, but must be dealt with in the same way. The period equation is cubic, and so there are three relations between the h's to get the frequencies right. Next, with each of these frequencies in turn, we must find the normal coefficients and so determine ζ_4 as a sum of terms in u_4, u_5, u_6 with coefficients which are functions of the h's. The squared moduli of these coefficients must be in the ratios $3:\frac{3}{2}:\frac{1}{2}$, and this gives two further conditions. There are not enough in all to fix the h's, and I have therefore merely selected a set which will satisfy all the conditions, taking them purely real for convenience. The equations become

$$\left.\begin{aligned} (-\kappa+\beta+\tfrac{1}{4}\omega)\zeta_4+\frac{1}{4}\sqrt{\frac{3}{10}}\omega\zeta_5+\frac{1}{4}\sqrt{\frac{3}{2}}\omega\zeta_6&=\frac{\sqrt{5}}{3}eZ,\\ \frac{1}{4}\sqrt{\frac{3}{10}}\omega\zeta_4+(-\kappa+\beta+\tfrac{7}{8}\omega)\zeta_5+\frac{3}{8\sqrt{5}}\omega\zeta_6&=0,\\ \frac{1}{4}\sqrt{\frac{3}{2}}\omega\zeta_4+\frac{3}{8\sqrt{5}}\omega\zeta_5+(-\kappa+\beta+\tfrac{3}{8}\omega)\zeta_6&=0. \end{aligned}\right\} \quad \ldots\ (15{\cdot}5)$$

The next stage is to bring in the strong effect, which depends on the coefficients h_{12}, h_{14}, h_{25}, etc. We have relations

$$\tfrac{1}{3}h_{11}+\frac{1}{\sqrt{3}}h_{12}+\frac{\sqrt{5}}{3}h_{14}=0, \text{ etc.},$$

from (7·11) These are quite insufficient to determine all

the h's. I therefore proceeded differently. Leaving them all undetermined the equations were transformed by means of (14·1) to their final form, a very heavy piece of work, and then the conditions become simply that in the new equations $h_{1r}=0$. The remaining undetermined values were chosen to be all real, and so as to remove as far as possible the irrationalities in the expressions. It is possible that the choice could be improved, but as the whole cannot be supposed to have any real physical foundation it was not worth going through the considerable labour of hunting for better values. The final equations are given; it would be quite straightforward to put down the L from which they are derived.

$$\zeta_1(-\kappa) + \zeta_4(-\beta) + \zeta_5\left(\frac{\beta}{\sqrt{3}}\right) = eZ,$$

$$\zeta_2(-\kappa+\omega) + \zeta_3\left(-\beta-\frac{1}{16}\omega\right) + \omega\zeta_4\left(-\frac{3\sqrt{3}}{40} + \frac{3}{40\sqrt{2}} + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \omega\zeta_5\frac{1}{10}\sqrt{\frac{3}{2}} + \omega\zeta_6\frac{3\sqrt{3}}{40} = 0,$$

$$\zeta_2\left(-\beta-\frac{1}{16}\omega\right) + \zeta_3\left(-\kappa+\frac{5}{8}\omega\right) + \omega\zeta_4\left(\frac{3\sqrt{3}}{40} - \frac{3}{40\sqrt{2}} + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \omega\zeta_5\left(-\frac{1}{10}\sqrt{\frac{3}{2}}\right) + \omega\zeta_6\left(-\frac{3\sqrt{3}}{40}\right) = 0,$$

$$\zeta_1(-\beta) + \omega\zeta_2\left(-\frac{3\sqrt{3}}{40} + \frac{3}{40\sqrt{2}} + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \omega\zeta_3\left(\frac{3\sqrt{3}}{40} - \frac{3}{40\sqrt{2}} + \frac{1}{4}\sqrt{\frac{3}{2}}\right) + \zeta_4\left[-\kappa+\omega\left(\frac{21}{40} - \frac{3}{10}\sqrt{\frac{3}{2}}\right)\right] + \zeta_5\left[\frac{\beta}{\sqrt{3}} + \omega\left(-\frac{\sqrt{3}}{40} - \frac{9}{20\sqrt{2}}\right)\right] + \omega\zeta_6\left(-\frac{3}{40}\right) = 0.$$

$$\zeta_1\left(\frac{\beta}{\sqrt{3}}\right) + \omega\zeta_2\frac{1}{10}\sqrt{\frac{3}{2}} + \omega\zeta_3\left(-\frac{1}{10}\sqrt{\frac{3}{2}}\right) + \zeta_4\left[\frac{\beta}{\sqrt{3}} + \omega\left(-\frac{\sqrt{3}}{40} - \frac{9}{20\sqrt{2}}\right)\right] + \zeta_5\left(-\kappa+\frac{11}{40}\omega\right) + \zeta_6\left[\frac{2}{\sqrt{3}}\beta + \omega\left(-\frac{\sqrt{3}}{8} + \frac{9}{20\sqrt{2}}\right)\right] = 0,$$

$$\omega\zeta_2\frac{3\sqrt{3}}{40} + \omega\zeta_3\left(-\frac{3\sqrt{3}}{40}\right) + \omega\zeta_4\left(-\frac{3}{40}\right) + \zeta_5\left[\frac{2}{\sqrt{3}}\beta + \omega\left(-\frac{\sqrt{3}}{8} + \frac{9}{20\sqrt{2}}\right)\right] + \zeta_6\left[-\kappa-\beta+\omega\left(\frac{63}{40} + \frac{3}{10}\sqrt{\frac{3}{2}}\right)\right] = 0. \quad . \quad . \quad . \quad (15·6)$$

In these equations κ stands for $p-p_0-\omega$. We cannot claim any physical reality for them; but merely that they do satisfy all the known conditions of a triplet while having only one active electron, after the manner suggested by the quantum theory.

The general balance of evidence would seem to be against the physical significance of mechanical models. We have seen how Voigt's model can be transformed in such a way that it can be given a physical meaning—at any rate as significant as is possible within the limitations of the classical theory; but this success is vitiated by its failure to accommodate Landé's calculations of the frequencies in fields of intermediate strength. The behaviour of such lines as the mercury line $1S-2p$ can definitely not be explained by a similar model, without introducing complications which would destroy much of its simplicity; and the magnetic gyration of ordinary substances also raises difficulty. Finally, though not conclusively, I have had no success in obtaining arithmetical simplicity for the corresponding model of the triplet.

On the other hand, it is possible to construct more general types of model which will meet these difficulties and which are mathematically useful in the calculation of gyration. They suggest the possibility of experiments which, using fields of practicable strength, should yield new information about the optical effects of magnetism.

Edinburgh, May 1925.

XII *On the Analysis of Certain Molecular Spectra.* *By* David M. Dennison, *Ph.D., University of Michigan* *.

In recent years much important work has been accomplished in interpreting molecular spectra by means of the quantum theory, and especially in obtaining information regarding the structure of the molecule through an examination of the positions and fine structure of the infra-red bands. Somewhat further light may be thrown upon this question through a consideration of the intensities of the bands with the aid of the correspondence principle.

In a recent article † I have investigated the molecular vibrations and infra-red spectrum of CH_4, and in this paper it

* Communicated by Prof. N. Bohr.

† D. M. Dennison, Astrophys. Journ. lxii. p. 84 (1925)

is intended to discuss from a similar point of view the infra-red spectra of the hydrogen halides, of CO_2, and of NH_3. No attempt has been made in this work to enter into the question of the origin of the forces holding the molecule in equilibrium, but the assumption has been made that the behaviour of the nuclei in the neighbourhood of their equilibrium positions may be described by means of central forces acting between them. This assumption, which is rigorously valid for the diatomic molecules, imposes in the case of a polyatomic molecule certain limitations in regard to the character of the equilibrium of the system. For the molecules considered in this note, where the number of degrees of vibrational freedom is just equal to the number of lines connecting the nuclei, the assumption as to central forces imposes the condition that there shall exist an equilibrium of the forces between each pair of nuclei. It is thought that the examination of the motion of such a simple model may suffice for the general interpretation of the character of the vibration to be associated with each band.

§ 1. *Molecular Vibrations.*

The bands of the infra-red spectra as observed experimentally are found to consist of finite regions of absorption which in certain cases have been resolved into a series of fine structure lines due to the rotation of the molecule. It is easily shown * that the integral of the observed absorption coefficient α_ν over the region of the band in question is connected in the following way with the Einstein probability coefficient A_0^i of spontaneous transition from the state ν_i to the normal or vibrationless state,

$$A_0^i = \frac{g_0}{g_i}\nu_i^2 K \int_0^\infty \alpha_\nu \, d\nu,$$

where g_0 and g_i are the *à priori* probabilities of the normal state and of the state ν_i respectively, and K is independent of ν_i. Since the absorption coefficient α_ν is the quantity which is observed experimentally, it will be convenient to employ as a measure of intensity ρ_i^2, defined by the relation

$$\rho_i^2 = \frac{A_0^i}{\nu_i^2} = \frac{g_0}{g_i} K \int_0^\infty \alpha_\nu \, d\nu. \quad . \quad . \quad . \quad . \quad (1)$$

In many cases, due to the experimental difficulties in

* Füchtbauer, *Phys. Zeit.* xxi. p. 322 (1920); R. Tolman, Phys. Rev. xxiii. p. 693 (1924).

determining the form of the absorption curves, it is inaccurate to compute the integral of the absorption coefficient over the region. It is evident, however, that when we compare absorption bands of the same molecule for which the electric moment vibrates in the same direction, the effective moment of inertia will be the same for each band, and hence if the absorption curves are plotted to a scale of frequencies as abscissæ, they will be everywhere proportional in their ordinates. Thus, if we compare two curves of this sort, the integral may be replaced by the absorption coefficient at some characteristic point, as, for example, its maximum value $(\alpha_\nu)_m$. It is unfortunate that there are so few accurate data available as to the experimental values of the intensities of the infra-red bands. This is possibly due both to the difficulty in obtaining them and to the fact that in the past the greatest interest has been centered on the positions of the lines and not upon their relative intensities. For that reason the experimental values given in this paper seem in general to have an accuracy which is no better than 10 or 20 per cent., and in a few cases may well be worse.

A comparison between the experimental value of ρ_i^2 as determined by (1), and a theoretical estimate of this quantity is obtained through a consideration of the motion of the electric moment of the model. In accordance with the previous assumption as to central forces acting upon the nuclei, it will now be assumed that each nucleus may be thought of as the centre of an effective charge, and that hence the change of electric moment is directly proportional to the displacement of the particles relative to the centre of gravity of the system. If E_i be the amplitude of the change of the electric moment, as is well known, the correspondence principle yields the following relation which in general is rigorously valid only in the region of large quantum numbers:

$$A_0^i(h\nu_i) = gE_i^2\nu_i^4 ;$$

and hence

$$\rho_i^2 = \frac{A_0^i}{\nu_i^2} = E_i^2\nu_i(\text{const.}) \quad . \quad . \quad . \quad . \quad (2)$$

In using this equation in the following sections it will be assumed that the amplitude of the change of the electric moment E_i is to be taken in the upper state rather than an average value between the two states to be connected with the transition. Such a procedure seems to be entirely justified in comparing the intensities of the fundamental vibration bands of a given system, since the relative values

of ρ_i^2 will be approximately independent of any type of average of E_i which might be taken. On the other hand, in comparing the intensity of a fundamental with that of its harmonics, appreciable errors may enter due to this cause, but it has been thought best even here to use the value of E_i in the upper state since in all cases the transition is to the zero or vibrationless state.

In considering the general characteristics of the vibratory motion of a molecule, an essential simplification of the problem may be made by assuming the amplitude of vibration to be infinitesimal; an assumption which, as is well known from the experimental positions of the harmonic bands of diatomic and other molecules, will not introduce any appreciable errors as regards the values of the fundamental frequencies. A system of n-particles will in general have $3n$ degrees of freedom, but of these three degrees may be associated with a translation of the system as a whole and (for $n>2$) three degrees with a rotation of the system, and hence there are left only $3n-6$ degrees of internal or vibrational freedom. While an analysis of the motion may be carried out using $3n$ coordinates, it seems preferable in the present case, where the displacements of the particles are infinitely small, to use only $(3n-6)$ coordinates, ignoring from the outset those coordinates which define the translation and rotation of the system. Such an ignoration may easily be effected by allowing only such displacements of the particles in space for which, in an imagined state of motion where the velocities of the particles are proportional to the displacements in question, the linear and angular momenta of the system are equal to zero. Under these conditions the potential and kinetic energies may be expressed as positive definite quadratic forms in the $(3n-6)$ coordinates and their time derivatives respectively and, through the transformation to the so-called normal coordinates, the normal or fundamental frequencies of the system may be determined.

Since the amplitude of vibration is assumed to be infinitesimal the electric moment in any direction R_θ may be expressed as a linear function of the $(3n-6)$ original coordinates, and hence also of the normal coordinates which are connected to the original coordinates by linear transformations. Thus,

$$R_\theta = \sum_1^u B_{\theta i} \cos(2\pi\nu_i t + \gamma_i),$$

where $\nu_1, \ldots \nu_u$ are the normal frequencies. A simple application of the correspondence principle makes it evident that,

according to the quantum theory, just as in the classical theory, only the frequencies $\nu_1, \ldots \nu_u$ may be absorbed or emitted, and that hence the system is equivalent to a number u of independent Planck oscillators whose characteristic frequencies are directly the normal frequencies of vibration. As is well known, such a simplified system does explain the essential features of the observed infra-red spectra, consisting mainly as they do of a series of prominent fundamental frequencies which are independent of each other. The appearance of harmonic and combination bands is conditioned by a divergence of the motion of the molecule from infinitesimal motion, and the problem of their intensity will be treated in the following section.

§ 2. *Diatomic Molecules. Intensity of Harmonic Bands*

The diatomic molecule possesses one degree of vibrational periodicity and one degree of rotational periodicity. In the first approximation, when the amplitude of vibration is taken to be infinitesimal and the moment of inertia constant during transition, the spectrum reduces to one band, the fundamental, whose fine structure consists of a series of lines linearly spaced as regards frequency. The theoretical frequencies of the harmonic bands, whose intensities are, however, zero under these assumptions, would be exact multiples of the frequency of the fundamental band. The true finite and anharmonic character of the motion is shown in the fact that the observed fine structure lines are not exactly linearly spaced, but are crowded together on one side of the band. Moreover, the harmonic bands appear with finite intensity and their frequencies are not exact multiples of the fundamental but are given by the following relation, where x is a small constant characteristic of the potential energy function:

$$\nu = n\nu_0(1-nx).$$

As is well known, Kratzer * has been able, by quantizing the motion of a rotating anharmonic oscillator, to account satisfactorily for the positions of the fine structure lines, and from the observations of Imes † on the hydrogen halides to determine the potential energy function for these substances. In the present section the attempt will be made to compare the relative intensities of the fundamental and harmonics

* A. Kratzer, *Zeit. f. Phys.* iii. p. 289 (1920).
† E. S. Imes, Astrophys. Journ. l. p. 251 (1919).

through the use of the constants of the potential energy function just mentioned.

Let the kinetic and potential energies be expressed as follows, where μ, K, K_2, and K_3 are constants, and X the normal variable representing the displacement of the nuclei from their equilibrium positions:

$$T = \tfrac{1}{2}\mu\dot{X}^2,$$

$$U = \frac{K}{2}X^2 + \frac{K_2}{3}X^3 + \frac{K_3}{4}X^4.$$

The following equations have been derived by Kratzer (*l. c.*) and by Hettner *, giving the approximate solution of the energy equations:

$$X = A\cos 2\pi\nu t + \frac{K_2A^2}{6K}\cos 4\pi\nu t + \left(\frac{K_2^2}{6K^2} + \frac{K_3}{4K}\right)\frac{A^3}{8}\cos 6\pi\nu t - \frac{K_2A^2}{2K},$$

$$\nu = \nu_0\left\{1 - \frac{A^2}{24}\left[10\left(\frac{K_2}{K}\right)^2 - \frac{9K_3}{K}\right]\right\},$$

$$T + U = nh\nu_0\left\{1 - \frac{A^2}{48}\left[10\left(\frac{K_2}{K}\right)^2 - \frac{9K_3}{K}\right]\right\} = nh\nu_0(1 - xn),$$

where $$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \quad \text{and} \quad A^2 = \frac{nh}{2\pi^2\mu\nu_0}.$$

According to equation (2) the intensities of the fundamental and first and second overtones to a high approximation become respectively, ignoring the constant,

$$\rho_1^2 = A_0^2\nu_0,$$

$$\rho_2^2 = \left(\frac{K_2}{6K}\right)^2(4A_0^4)(2\nu_0) = \frac{2}{9}\left(\frac{K_2}{K}\right)^2 A_0^4\nu_0,$$

$$\rho_3^2 = 81\left(\frac{K_2^2}{48K^2} + \frac{K_3}{32K}\right)^2 A_0^6\nu_0,$$

where $$A_0^2 = \frac{h}{2\pi^2\mu\nu_0}.$$

In computing the above values there is involved an uncertainty which is inherent to all the usual applications of the correspondence principle to the question of intensities,

* G. Hettner, *Zeit. f. Phys.* i. p. 351 (1920).

namely, the uncertainty as to which value of the amplitude E_i shall be used in equation (2). As has been mentioned, it has been assumed in the present work that the amplitude in the higher state is to be used, since each transition is to the zero or vibrationless state.

We may compare the theoretical intensities with the intensities found experimentally in the case of the halogen halides, through the use of equation (1).

	$\frac{K_2A_0}{K}$.	$\frac{\rho_2^2}{\rho_1^2}$ (Theo.).	$\frac{\rho_2^2}{\rho_1^2}$ (Exp.).
HBr	−·412	·038	·05
HCl	−·443	·044	·06
HF.....	−·475	·050	—

The values of $\frac{K_2A_0}{K}$ depend upon the experimental work of Imes (*l. c.*) for HBr and HF and upon that of Colby, Meyer and Bronk * for HCl. The experimental value of $\frac{\rho_2^2}{\rho_1^2}$ is obtained from the work of Brinsmade and Kemble † for HCl, while for HBr it is necessary to combine their work with that of Burmeister ‡.

Since the constant $\frac{K_2A_0}{K}$ depends upon a knowledge of the fine structure which is in most cases unknown, it is impossible to test the intensities generally by the methods given above. There does, however, exist a relation between ρ_1^2, ρ_2^2, ρ_3^2 and x, which may in certain cases be tested experimentally. Thus the position of the centre of each band ν_i is given by

$$\nu_i = \nu_0 n_i(1 - x n_i),$$

where evidently

$$x = \frac{A_0^2}{48}\left[10\left(\frac{K_2}{K}\right)^2 - 9\frac{K_3}{K}\right].$$

The relation between the constants in question is found by direct substitution to be

$$x = \frac{3}{2}\frac{\rho_2^2}{\rho_1^2} - \frac{2}{3}\left(\frac{\rho_2}{\rho_1}\right)\left(\frac{\rho_3}{\rho_2}\right).$$

* Colby, Meyer & Bronk, Astrophys. Journ. lvii. p. 7 (1923).
† J. Brinsmade & E. C. Kemble, Proc. Nat. Acad. iii. p. 420 (1917).
‡ B. Burmeister, *Verh. d. D. phys. Ges.* xv. p. 589 (1913).

This formula may be tested to a certain extent in the case of CO, where, according to Burmeister (*l. c.*),

$$x = \cdot 006,$$

$$\frac{\rho_2^2}{\rho_1^2} = \cdot 031.$$

Hence, solving for $\frac{\rho_3^2}{\rho_2^2}$, we find

$$\frac{\rho_3^2}{\rho_2^2} = \cdot 12.$$

C. Schaefer and M. Thomas * have found experimentally the second overtone of CO and give as a measure of its relative intensity 1 : 14·3, as compared with the first overtone. Taking this as a measure of $\frac{\rho_3^2}{\rho_2^2}$, we have,

$$\frac{\rho_3^2}{\rho_2^2} = \cdot 07.$$

§ 3. *Symmetrical Triatomic Molecules.*

In considering the vibration spectrum of a triatomic molecule of the general type XY_2, it does not seem possible, without some further assumption as to the structure, to determine uniquely the form of the molecule from the positions of the fundamental infra-red bands whose number is at most three. In the present treatment it will be assumed that the Y-atoms are equidistant from the X-atom, and that in general the three atoms do not lie along a straight line. Such an assumption does not seem inconsistent with the general chemical and physical evidence as to the structure of such molecules and in the case of H_2O is directly in accord with a recent investigation by Hund †, in which the equilibrium states of this molecule among others were examined under the assumption that the electronic configuration is central about the oxygen nucleus, with the exception of a polarization induced by the presence of the hydrogen nuclei.

If the assumption mentioned previously is made, that the fields of force are central about each atom, the potential

* C. Schaefer & M. Thomas, *Zeit. f. Phys.*, xii. p. 330 (1923).
† F. Hund, *Zeit. f. Phys.* xxxi. p. 81 (1925).

energy function for infinitesimal displacements reduces to the following simple form :

$$W = \frac{K}{2} q_1^2 + \frac{K'}{2}(q_2^2 + q_3^2),$$

where K and K′ are constants, q_1 the mutual displacement of the Y-particles relative to each other, and q_2 and q_3 the mutual displacements of the X-particle relative to each Y-particle respectively. As original coordinates it has, however, been found more convenient to choose q, x, y, where q is equal to q_1 as just defined, and x and y are the displacements in rectangular coordinates of the X-particle relative to the centre of gravity of the Y-particles. Let M be the mass of the X-particle, and m that of each Y-particle, and let α be the half angle at the apex of the isosceles triangle formed by the three particles. The potential and kinetic energies for infinitesimal displacements may be found quite simply by allowing a variation of each coordinate to occur independently, and by examining the total resulting displacement of each particle under the conditions that there shall be no rotation or translation of the molecule as a whole. As is well known, the energy functions allow a determination of the normal frequencies of the system as a function of the roots of a characteristic determinant *, which in the present case may be written in the following form :

$$\left[\frac{m\lambda}{K'} - 1 - \frac{2m}{M}\sin^2\alpha\right]\left[\left(\frac{m\lambda}{K'}\right)^2 - 2\left(\beta + \tfrac{1}{2} + \frac{m}{M}\cos^2\alpha\right)\frac{m\lambda}{K'} + \frac{2\beta}{\mu}\cos^2\alpha\right] = 0,$$

where

$$\beta = \frac{K}{K'}$$

and

$$\mu = \frac{M}{2m + M}.$$

The system is evidently non-degenerate since the above determinant contains three independent roots, which we shall denote by λ_1, λ_2, and λ_3 respectively, leading to three frequencies †, ν_1, ν_2, and ν_3, where

$$\nu_i = \frac{1}{2\pi}\sqrt{\lambda_i}.$$

* See, for example, E. T. Whittaker, 'Analytical Dynamics,' 2nd edition, p. 178.

† In addition to considering the equilibrium of the molecule of H_2O, Hund (*l. c.*) has computed its normal frequencies of vibration under the assumptions mentioned previously. The frequency functions obtained by him may be directly transformed into the normal frequencies given here by allowing the coefficients referring to the polarization to vanish.

An examination of the character of motion to be associated with each normal mode of vibration may be made through a consideration of the linear equations connecting the so-called normal coordinates with the original coordinates q, x, y. In the motion corresponding to the vibration ν_1, where λ_1 is the linear root of the determinant, it is found that the X-particle vibrates in the plane of the triangle along a line perpendicular to the symmetry line while the distance between the Y-particles remains unchanged*. In the motion corresponding to either ν_2 or ν_3 the X-particle vibrates along the line of symmetry, while the Y-particles in their motions always preserve a symmetry about this line.

As has been mentioned, the change of the electric moment is assumed to depend directly upon the displacements of the particles, and in the present case will be proportional to the displacement of the X-particle relative to the centre of gravity of the Y-particles; that is, it will have components proportional to the original coordinates x and y. The intensity ρ_i^2 as defined by equation (2) may now be found, with the aid of the linear equations referred to above, to have the values

$$\rho_1^2 = \frac{C}{2\mu + \frac{2\mu^2}{\tan^2\alpha}},$$

$$\rho_j^2 = \frac{C}{2\mu + \frac{1}{2}\left(\frac{\sin\alpha\cos\alpha}{\frac{m\lambda_j}{2K'} - \beta - \frac{1}{2}\sin^2\alpha}\right)^2},$$

$j = 2, 3.$

The problem of the normal frequencies of the CO_2 molecule was attacked in a most successful manner by N. Bjerrum† in 1914 through the use of assumptions which were identical with those employed here, and which lead to identical frequency functions. By correlating the observed spectrum of CO_2 with the theoretical frequencies he obtained two solutions yielding two very different values for α—72°·5 and 20°·3,—between which he was not able to decide at that time. It is found upon computing the intensities that the latter solution, $\alpha = 20°{\cdot}3$, is entirely inconsistent with the experimental data, whereas the theoretical values for the intensities seem in quite good agreement with

* It is to be noted that K does not enter the expression for ν_1.

† N. Bjerrum, *Verh. d. D. phys. Ges.* xvi. p. 737 (1914).

experiment under the former solution, where $\alpha = 72°{\cdot}5$, and in the following work only this solution will be considered.

Many investigators have examined the near infra-red spectrum of CO_2 and have found it to consist of three bands lying at $2{\cdot}74\,\mu$, $4{\cdot}25\,\mu$ and $14{\cdot}66\,\mu$, with almost no absorption between these regions. In the following, the work of W. W. Coblentz * will be used both for determining the positions of the bands and their relative intensities as given by equation (1). Since there are three constants—K, K′, and α—the positions of the three bands are just sufficient for their determination.

The constants entering the intensity expressions are so chosen that the sets agree at the longest wave-band :

$$\alpha = 72° 37',$$
$$K = 554 \times 10^4,$$
$$K' = 151 \times 10^4.$$

	Frequency (Theo.).	Frequency (Obs.).	Direction of vibration of electric moment relative to symmetry line.	ρ_i^2 (Theo.).	ρ_i^2 (Obs.).
ν_1	705×10^{11}	705×10^{11}	$\perp$	1·8	2·0
ν_2	1095×10^{11}	1095×10^{11}	$\parallel$	0·01	0·5
ν_3	205×10^{11}	205×10^{11}	$\parallel$	1·8	1·8

The agreement between the theoretical and observed frequencies is, of course, no direct verification of the theoretical model, since there are just as many constants entering the theoretical expressions as there are frequencies. On the other hand, the values of the relative intensities depend only upon the constants K, K′, and α, which have been entirely determined from the positions of the bands. It is seen that the theoretical prediction of two strong bands ν_1 and ν_3, of about equal intensity, and one weak band ν_2 is qualitatively in accord with the observations, although the exact value of the intensity of this latter is somewhat in error. While this is no doubt due mainly to a failure of the theoretical assumptions, it may also in some degree be due to the experimental difficulty of determining accurately the intensity of a very weak band.

Before turning to the question of the fine structure of the

* W. W. Coblentz, 'Investigations of Infra-red Spectra,' Part I., Carnegie Institute of Washington, D. C. (1905).

CO_2 bands, a few remarks may be made concerning the type of molecule predicted by the above correlation. Unfortunately, the number of observed bands does not decide between a symmetrical and a non-symmetrical model, since either in general possesses three independent frequencies of vibration. In the particular case, however, when the three atoms lie in a straight line with the oxygens symmetrically placed on either side of the carbon, the change of electric moment for one of the three vibrations will be zero, provided only the symmetry extends to the potential energy function, since for this vibration the original symmetry of the model is preserved at every instant in the motion. Thus the fact that three bands of finite intensity are observed seems to remove the possibility that the particles can be symmetrically located along a straight line.

On the other hand, from measurements of the dielectric constant of CO_2, H. Weigt* has determined the electric moment of the molecule in the normal state and has found it to have a very small value—about $\frac{1}{15}$ the corresponding value for the HCl molecule. This result seems to give a certain support to the theoretical model, since if α has a value as large as $72°{\cdot}5$, the carbon atom is not greatly displaced from the line of the oxygen atoms, and hence the electric moment might be expected to have a small value as compared, for example, with the electric moment of HCl.

While nothing definite can be said with regard to the values of K and K′, it may be of interest to compare the value of K′ for the carbon-oxygen bond in CO_2 with the value of K′ for the bond in carbon monoxide. Such a comparison is only justified in the sense that if the fields of force are central in CO_2, then there must exist an equilibrium of the forces between each two particles just as for the case of a diatomic molecule, and hence to a first approximation the potential energy function may be the same for the C—O bond in both CO_2 and CO. The spectrum of CO consists of one fundamental band at $4{\cdot}66\,\mu$ and its harmonics. The constant K′ may be found from the following equation, where μ is the reduced mass of the carbon and oxygen atoms:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K'}{\mu}}.$$

Substituting, we find $K' = 184 \times 10^4$, a value which is in quite fair agreement with the corresponding value $K' = 151 \times 10^4$ deduced from the CO_2 spectrum.

* H. Weigt, *Phys. Zeit.* xxii. p. 643 (1921).

E. F. Barker * has investigated with high dispersion the bands corresponding to ν_1 and ν_2. The second of these at $4{\cdot}25\,\mu$ he found to consist of a rather close doublet, the distance between whose maxima he gives to be $9{\cdot}12 \times 10^{11}$ waves per sec. The band at $2{\cdot}74\,\mu$ was resolved into four maxima giving the appearance of two doublets. The position of these maxima, which seem in themselves about to be resolved into fine lines, he gives to be 1080·7, 1089·7, 1111·9, and $1120{\cdot}6 \times 10^{11}$ waves per sec.

In the theoretical model considered above, where $\alpha = 72^\circ\,37'$, the principal moments of inertia have the following values where A is the moment of inertia about the axis, lying in the plane of the particles and perpendicular to the symmetry line :

$$A = A,$$
$$B = 37{\cdot}4\,A,$$
$$C = 38{\cdot}4\,A.$$

It is clear that to a first approximation the model may be thought of as possessing an axial symmetry about the A-axis, which we shall now call the figure-axis. As is well known, the quantum conditions become very simple when B = C and the rotational energy assumes the following value :

$$E_r = \left[\frac{m^2}{C} + \left(\frac{1}{A} - \frac{1}{C}\right)n^2\right]\frac{h^2}{8\pi^2},$$

where $n \leqq m$.

Consider first the band ν_1 at $4{\cdot}25\,\mu$. The electric moment, according to the theoretical model, vibrates along the figure-axis, and an expansion of the motion in a trigonometric series shows, with the aid of the correspondence principle, that only the following transitions may occur † :

$$\begin{cases} \triangle m = 0, \\ \triangle n = 0, \end{cases} \qquad \begin{cases} \triangle m = \pm 1, \\ \triangle n = 0. \end{cases}$$

The first of these sets of transitions would give rise to a zero branch, but it is easily seen that the intensities of its lines are proportional to $\frac{n^2}{m^2}$, whereas the intensities of the

* E. F. Barker, Astrophys. Journ. lv. p. 391 (1922).

† The complete expansion of the motion in a trigonometric series appears in the author's paper on methane, mentioned previously.

lines to be associated with the second set of transitions are proportional to $\frac{m^2-n^2}{m^2}$. On account of the fact that $\frac{1}{A} \gg \frac{1}{C}$, it is evident, from the function for E_r, that in a state of temperature equilibrium the most probable values for n will be very much smaller than those for m, and hence it is to be expected that the total intensity of the zero branch will be very small and might well have escaped Barker's observations. On the other hand, the second set of transitions gives rise to a positive and negative branch not unlike the fine structure observed for the diatomic gases. While Barker was unable to resolve the individual lines, he was able to compute the moment of inertia in the well-known manner from the separation of the maxima of intensity of the two branches. He gives the following result :—

$$B \cong C \cong 48{\cdot}6 \times 10^{-40} \text{ gm. cm.}^2.$$

Using this value in conjunction with that of α obtained from the theoretical model, we may compute the distance between the oxygen nuclei to be $1{\cdot}92 \times 10^{-8}$ cm. and the distance between the carbon nucleus and the centre of gravity of the oxygen nuclei to be $0{\cdot}30 \times 10^{-8}$ cm.

In the motion corresponding to the band ν_2 at $2{\cdot}74\ \mu$, the model predicts that the electric moment vibrates perpendicular to the figure-axis. It may be shown that the only possible transitions are,

$$\begin{cases} \triangle m = 0, \\ \triangle n = \pm 1, \end{cases} \qquad \begin{cases} \triangle m = \pm 1, \\ \triangle n = \pm 1, \end{cases}$$

giving rise to the following sets of lines :

$$\nu = \left(\frac{1}{A} - \frac{1}{C}\right)(\pm 2n+1)\frac{h}{8\pi^2},$$

$$\nu = \left\{ \frac{1}{C}(\pm 2m+1) + \left(\frac{1}{A} - \frac{1}{C}\right)(\pm 2n+1) \right\} \frac{h}{8\pi^2}.$$

These lines may evidently be thought of as a series of lines whose spacing is $\left(\frac{1}{A} - \frac{1}{C}\right)\frac{h}{4\pi^2}$, upon which spacing is superimposed a second set of lines of spacing $\frac{1}{C}\frac{h}{4\pi^2}$. This corresponds well with the observed fine structure when we remember that $\frac{1}{A} \gg \frac{1}{C}$. In correlating theory and

experiment it becomes necessary to assume that the positions of the lines of spacing $\left(\frac{1}{A}-\frac{1}{C}\right)\frac{h}{4\pi^2}$ coincide with the centres of the two doublets, whereas each of these doublets in itself is due to the envelope of unresolved lines of spacing $\frac{1}{C}\frac{h}{4\pi^2}$. Such a view is strengthened by the fact that the separation of the maxima of these doublets is, within experimental error, equal to the separation of the doublet in the band at $4{\cdot}25\,\mu$, which is due wholly to lines of spacing $\frac{1}{C}\frac{1}{4\pi^2}$. The great energy involved in changes of the quantum number n explains why at ordinary temperatures no further lines of this series were observed. If, from analogy with the hydrogen halide spectra, we assume that the series of lines of spacing $\left(\frac{1}{A}-\frac{1}{C}\right)\frac{h}{4\pi^2}$ has a gap of one missing line in the centre *, the moment of inertia A may be computed to be

$$A = 1{\cdot}05\times10^{-40}\ \text{gm. cm.}^2.$$

The experimentally observed spectrum leads to a ratio $\frac{C}{A}=46$, which seems to be in good agreement with the theoretical value of about 38.

§ 4. *Axially Symmetrical Molecules with Four Atoms.*

In the present section we shall consider the vibration spectrum of a molecule of the type XY_3. The assumption will be made that in the normal state of the molecule the X-atom is equidistant from each of the Y-atoms which themselves lie at the corners of an equilateral triangle. It is further assumed that the X-atom does not lie in the plane of the Y-atoms. If, as before, the fields of force are taken to

* The number of missing lines at the centre cannot be ascertained until more lines of the series of spacing $\left(\frac{1}{A}-\frac{1}{C}\right)\frac{h}{4\pi^2}$ are found experimentally. It is quite possible that there is no gap in the centre of the band, in which case the value of A will be about half that given above and the value of $\frac{C}{A}$ will not check as well with the theoretical model.

be central about each atom, the potential energy function for infinitesimal displacements becomes

$$W = \frac{K}{2}(q_1^2 + q_2^2 + q_3^2) + \frac{K'}{2}(q_4^2 + q_5^2 + q_6^2),$$

where q_1, q_2, and q_3 are the displacements of the Y-particles relative to each other, and q_4, q_5, and q_6 the displacements of the X-particles relative to each of the Y-particles respectively.

As original coordinates we shall choose q_1, q_2, q_3 giving the displacements of the Y-atoms relative to each other, and x, y, z giving the displacement of the X-atom along rectangular axes relative to the centre of gravity of the Y-atoms. The kinetic and potential energies for infinitesimal displacements are deduced in a manner similar to that for the triatomic model, namely, by allowing variations of the coordinates q_1, q_2, q_3, x, y, z to occur independently and by examining the total displacements of each particle both in space and relative to each other under the conditions of no rotation or translation of the system as a whole. Letting M be the mass of the X-atom, m that of each Y-atom, a the normal distance of the Y-atoms from each other, and c the normal distance of the X-atom from the plane of the Y-atoms, we find the following expression for the characteristic determinant:

$$\left[l^2 - 2\left(\frac{3}{2}\alpha + \frac{1}{6} + \frac{c^2}{2\mu a^2}\right)l + \frac{3\alpha c^2}{\mu a^2}\right]\left[l^2 - 2\left(\frac{3}{4}\alpha + \frac{1}{12} + \frac{b}{12\mu}\right)l + \frac{\alpha b}{4\mu}\right]^2 = 0,$$

where

$$l = \frac{m\left(c^2 + \frac{a^2}{3}\right)\lambda}{K'a^2}, \qquad \mu = \frac{M}{3m + M},$$

$$\alpha = \frac{K}{K'}\left(\frac{c^2 + \frac{a^2}{3}}{a^2}\right), \quad \text{and} \quad b = 1 + 6\mu\frac{c^2}{a^2}.$$

The roots of the determinant we shall call λ_1, λ_2, λ_3, and λ_4 respectively, where λ_3 and λ_4 are the double roots and where $\lambda_1 > \lambda_2$ and $\lambda_3 > \lambda_4$. The system is evidently degenerate, for, while it possesses six degrees of freedom, only four independent frequencies, ν_1, ν_2, ν_3, and ν_4 enter the motion *,

* One of the cases treated under very general assumptions by C. J. Brester ('Kristallsymmetrie und Reststrahlen,' Utrecht, 1923, p. 117) is that of the molecule considered in the present section. He finds that

where, of course,

$$\nu_i = \frac{1}{2\pi}\sqrt{\lambda_i}.$$

The linear transformations connecting the original co-ordinates with the normal coordinates were found in order to understand the nature of the motion corresponding to each normal mode of vibration. In the vibrations ν_1 or ν_2, the transformations show that the X-particle vibrates along the symmetry axis, while the Y-particles in their motion always remain symmetrical with respect to this axis. Since the corresponding roots are single roots, the motion is quite determined in terms of the above constants. In the motion correspon ling to ν_3 or ν_4, the X-particle always remains in a plane perpendicular to the symmetry axis. The roots λ_3 and λ_4 are double roots, and hence two arbitrary constants enter the motion. It may be sho vn that in this motion the X-particle moves in an ellipse whose eccentricity and orientation in the symmetry plane are determined by the arbitrary constants. The family of ellipses, however, are conditioned through the relation that the sum of the squares of their minor and major axes shall be a constant, which is a function of the quantum conditions.

As in the case of the triatomic molecule, we shall assume that the change of the electric m oment is proportional to the displacement of the X-particle relative to the centre of gravity of the Y-particles. The intensities as determined by equation (1) may now be computed, making use of the linear transformations referred to:

$$\rho_j^2 = \frac{\frac{c^2}{a^2}C}{3\mu\frac{c^2}{a^2} + \left[\frac{3\mu m\left(c^2+\frac{a^2}{3}\right)\lambda_j}{K'a^2} - \frac{3c^2}{a^2}\right]^2}, \qquad j=1,2.$$

$$\rho_K^2 = \frac{\frac{36}{b^2}\left[\frac{2}{3}\frac{m\left(c^2+\frac{a^2}{3}\right)\lambda_K}{K'a^2} - \alpha - \frac{1}{9}\right]^2 C}{\frac{4}{3} + \frac{(36)3\mu}{b}\left[\frac{2}{3}\frac{m\left(c^2+\frac{a^2}{3}\right)\lambda_K}{K'a^2} - \alpha - \frac{1}{9}\right]^2}, \qquad K=3,4.$$

where C is a constant.

there will exist four active frequencies—two single oscillations with electric moment vibrating along the symmetry axis, and two double oscillations—perpendicular to the axis, a result entirely in agreement with the present work.

The best existing data for a molecule of the type under consideration seem to be for the molecule of ammonia, NH_3. W. W. Coblentz (*l. c.*) has observed two very intense bands at $10{\cdot}7\,\mu$ and $6{\cdot}14\,\mu$, with a considerably weaker band at $2{\cdot}97\,\mu$, beyond which point he did not go. Lately K. Schierkolk * has re-examined a long range of the ammonia infra-red spectrum under high dispersion. In addition to the bands cited by Coblentz, he has found a band at $2{\cdot}22\,\mu$ of the same order of intensity as the band at $3{\cdot}0\,\mu$. Beyond this he found two bands at $1{\cdot}94\,\mu$ and $1{\cdot}49\,\mu$ whose intensity was about half that of the two bands immediately preceding. He observed, moreover, a series of very faint bands, many of which may evidently be thought of as combinations and harmonics of the intense bands †.

As has been shown, the theoretical model predicts only four frequencies, as indeed will any model of this sort which possesses an axis of symmetry ‡. Thus, if all six bands observed by Schierkolk are fundamental frequencies characteristic of the molecule NH_3, then the molecule does not have an axial symmetry. It seems, however, possible that the faintest two of the six observed bands may be due to traces of impurities or perhaps to associated or ionized molecules. In view of this possibility the correlation will be carried out, choosing as fundamental bands the four strongest bands, namely, at $10{\cdot}7\,\mu$, $6{\cdot}14\,\mu$, $2{\cdot}97\,\mu$, and $2{\cdot}22\,\mu$. The theoretical frequencies contain three constants, K, K′, and $\frac{c}{a}$, to determine which we shall use the three bands observed by both Coblentz and Schierkolk. Upon trying numerically

* K. Schierkolk, *Zeit. f. Phys.* xxix. p. 277 (1924).

† In a recent note G. Hettner (*Zeit. f. Phys.* xxxi. p. 273, 1925) has pointed out that, if the bands at $10{\cdot}7\,\mu$ and $6{\cdot}14\,\mu$ be taken as fundamental, the remaining bands, both faint and strong, to a fair approximation fall near the positions of the higher harmonics of the two fundamentals. This may perhaps be only a coincidence, however, since the relative intensities as well as the exact positions of these "harmonic" bands seem to differ rather much from what might be expected from a molecule whose motion is nearly harmonic.

‡ One of the cases treated by F. Hund (*l. c.*) is that of the equilibrium of the molecule of ammonia, where he has shown that, if the electronic configuration about the nitrogen, originally central, is capable of a polarization induced by the hydrogen nuclei, the molecule in the normal state must have just the axial symmetrical form assumed here. In considering the vibrations of such a molecule he erroneously states that there will exist only three active frequencies, whereas, unless the particles all lie in the same plane, there must in general exist four. The table of harmonic and combination bands given by him may easily be changed to take account of this, however, by allowing the band at $2{\cdot}97\,\mu$ (calculated $2\nu_2$) to become the fourth fundamental band.

all possible correlations it is found that only one leads to real values for constants, this leading to two solutions which lie quite close together. That is to say, within a certain range there may be a close correlation between three of the theoretical and experimental frequencies, and this correlation is considerably strengthened by finding that the fourth theoretical frequency lies very near to the fourth observed band. In the following table a set of values has been chosen for the constants which lies between the two solutions just mentioned with the view of slightly adjusting the values of the frequencies and also of the relative intensities. While this is rather arbitrary it can in no case make any great difference, since the functions change only by small amounts between the two solutions :

$$K = 27{\cdot}8 \times 10^4 \qquad \frac{c}{a} = 0{\cdot}255$$

$$K' = 36{\cdot}8 \times 10^4.$$

	Frequency (Theo.).	Frequency (Obs.).	ρ_i^2 (Theo.).	ρ_i^2 (Obs.).
ν_1 ∥	1335×10^{11}	1340×10^{11}	0·0076	0·12 —
ν_2 ∥	282	281	0·40	0·95 —0·84
ν_3 ⊥	1009	1009	0·056	0·060—0·065
ν_4 ⊥	488	474	0·251	0·251—0·251

In computing the observed intensities, the *à priori* probabilities of the states ν_3 and ν_4 are assumed to be twice those of the states ν_1 and ν_2, since the corresponding roots of the determinant λ_3 and λ_4 are double roots, whereas λ_1 and λ_2 are single. When two values of ρ_i^2 (obs.) are given, the first is from the work of Schierkolk and the second from that of Coblentz, where the constants have been so chosen that all intensities agree at the band ν_4, since here the experimental values seem most accurate.

While the theoretical and observed intensities do not check quite satisfactorily throughout the whole four bands, it is seen that, independently, for the bands corresponding to the same direction of vibration of the electric moment, that is ν_1 and ν_2 or ν_3 and ν_4, there is a fairly good agreement. This result will not appear surprising in the light of the discussion at the conclusion of this paper, where it is shown that the change of the electric moment may depend not only upon the absolute value of the displacements of the particles, but also to some

extent upon the directions of their displacements. In the present case no two of the vibrations are exactly similar, but pairs of vibrations having the same direction of oscillation of the electric moment will obviously resemble each other more closely than pairs for which this direction is different.

In the present paper no attempt will be made to go into the fine structure of these bands, although one remark may be made concerning the separation of the temperature maxima of the envelope of the fine structure lines. According to Schierkolk the most probable frequency of rotation for the band at 281 is greater than that for the band at 474 by a factor of about $\sqrt{2}$. This is, qualitatively at least, in agreement with the predictions of the model, since the vibration ν_2 is parallel to the symmetry axis and hence its fine structure depends only upon the smaller moment of inertia C, whereas the fine structure of the vibration ν_4, which is perpendicular to this axis, depends also upon the larger moment of inertia A. The ratio of A to C as given by the theoretical model is $\frac{A}{C} = 1{\cdot}51$.

§ 5. *The Absolute Value of the Absorption of the Fundamental Bands.*

In the present section we shall consider the absolute absorption of a harmonic oscillator of frequency ν_i, the amplitude of the oscillation of whose electric moment has the value $\epsilon_i E_i$. Equations (1) and (2) may be written as follows, where N is the number of molecules per unit volume in the normal state and the other symbols have their previous meanings:

$$A_0{}^i(h\nu_i) = \frac{8\pi h\nu_i{}^3 g_0}{c^2 N g_i} I_i, \quad . \quad . \quad . \quad . \quad . \quad (1')$$

where $I_i = \int_0^{\infty} \alpha_{\nu_i} d\nu_i$,

$$A_0{}^i(h\nu_i) = \tfrac{1}{3}(2\pi)^4 \frac{\epsilon_i{}^2}{c^3} \nu_i{}^4 E_i{}^2. \quad . \quad . \quad . \quad (2')$$

For convenience we may consider E_i to be the amplitude of vibration of the nuclei and ϵ_i their "effective" charge. Equating the last two relations and solving for ϵ^2, we have

$$\epsilon_i{}^2 = \frac{3hcg_0}{2\pi^3 N \nu_i g_i E_i{}^2} I_i. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the case of a diatomic molecule,

$$g_0 = g_i$$

and $$E_i^2 = \frac{h}{2\pi^2 \mu \nu_i},$$

where μ is the reduced mass of the nuclei.

Substituting *,

$$\epsilon_i^2 = \frac{3\mu c}{\pi N} I_i. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3\,a)$$

In the more general case of a polyatomic molecule, equation (3) takes the form

$$\epsilon_i^2 = \frac{3cMg_0}{\pi N F_i^2 g_i} I_i, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3\,b)$$

where M is a function of the masses of the nuclei and F_i is the factor connecting the amplitude of the electric moment with the amplitude of the normal coordinate X_i.

An accurate determination of ϵ_i by means of experimentally known values of I_i seems to be rather difficult, since, unfortunately, if the fine structure lines are narrow, much smaller than the slit width, the observed value of α_{ν_i} is less than its true value averaged over the region of the slit width. A study of the existing data seemed to show, however, that for the bands considered in this section the error introduced in I_i cannot be greater than that of a factor of 2, and hence that in ϵ_i is not greater than that of a factor 1·4. In the following table the values of the integral of the absorption coefficient I_i are estimated only, since errors due to this cause will be of a lower order of magnitude. The action of the incident radiation will not appreciably disturb the temperature equilibrium of the gas, and for all the cases treated in the table, N, the number of molecules per c.c. in the normal state, has been taken equal to the total number of molecules present per c.c.

* This formula might as well have been derived from the well-known relation that a linear oscillator absorbs an energy $\frac{e^2\pi}{3\mu}$ per second, independent of its amplitude. The fact that the two derivations lead to the same result depends upon using for E_i the amplitude of vibration in the upper state.

Substance.	$\frac{M}{F_i^2 \times 1{\cdot}65 \times 10^{-24}}$.	$\frac{g_0}{g_i}$.	$I_i \times 10^{-10}$.	Observer.	$\frac{\epsilon_i}{4{\cdot}77 \times 10^{-10}}$
HCl.....	0·973	1	71	E. v. Bahr*	0·075
			60	,, ,,	0·068
			52	Burmeister (*l. c.*)	0·064
					0·069
HBr.....	0·988	1	25 (?)	Burmeister	0·044 (?)
CO	6·86	1	27	Burmeister	0·123
			32	Coblentz (*l. c.*)	0·133
					0·128
CO_2	8·74	1	10·3	Coblentz	0·085
($\lambda = 14{\cdot}66\,\mu$)			12·7	Rubens and Aschkinass†	0·094
					0·090
NH_3.....	3·98	$\frac{1}{2}$	232	Coblentz	0·192
($\lambda = 6{\cdot}14\,\mu$)			250	Schierkolk (*l. c.*)	0·200
					0·196
CH_4‡	3·65	$\frac{1}{3}$	98	Coblentz	0·095
($\lambda = 7{\cdot}7\,\mu$)					

* E. v. Bahr, *Verh. d. D. Phys. Ges.* xxi. p. 115 (1913).

† Rubens & Aschkinass, *Ann. d. Phys. u. Chem.* lxiv. p. 584 (1898).

‡ The values of $\frac{M}{F_i^2}$ and $\frac{g_0}{g_i}$ are taken from the author's paper on methane, mentioned in the introduction.

In the above table the values in the column $\frac{\epsilon_i}{4{\cdot}77 \times 10^{-10}}$ are equal to the square root of the ratio of the observed absorption to the absorption of an oscillating dipole of charge unity ($4{\cdot}77 \times 10^{-10}$) and reduced mass $\frac{M g_0}{F_i^2 g_i}$. While it must always be remembered that ϵ is only a measure of the amplitude of oscillation of the electric moment, it may be of convenience to think of the observed absorption as being produced by the molecule in question whose nuclei are centres of effective charges ϵ_i. For the molecules CO_2, NH_3 and CH_4, the values given are to be associated with the C, N and C nuclei respectively, whereas the effective charge of each O, H and H nucleus is to be taken as $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{4}$ of the table values respectively.

While, as has been mentioned, the values given for I_i are

only approximate and may be somewhat too small, due to the narrow character of the fine structure lines, it is seen from the table that the observed absorption is of quite another order of magnitude from that which might be expected from a molecule whose nuclei possessed effective charges of unity. Thus, for example, in the case of HCl, if the electronic configuration was centrally symmetrical about the chlorine nucleus throughout the motion, the absorption should be about 210 times greater than that actually observed. Such a result seems to show that the central symmetry of the electrons about the chlorine ion has been essentially disturbed by the presence of the hydrogen nucleus, in such a way as to greatly lower the effective charge of the latter.

For the molecule of methane there exists some independent evidence which is directly in accord with the low values of the effective charge found here, for, in the author's paper on the methane spectrum, it has been shown that in order to obtain any correlation between the observed fundamental bands and the normal frequencies of the theoretical model, it is necessary to assume that the repulsive force acting between the hydrogen nuclei is a very small fraction of the force that would exist if the hydrogen nuclei possessed effective charges of unity and the electronic configuration was centrally symmetrical about the carbon nucleus.

In the case of HCl it may be of interest to compute the electric moment in the normal state, identifying for the moment the value of ϵ_i given in the table with the effective charge on the nuclei. The distance between the nuclei is known from the infra-red spectrum to be

$$d = 1{\cdot}265 \times 10^{-8} \text{ cm.},$$

and hence the electric moment

$$\mu = 1{\cdot}265 \times 0{\cdot}069 \times 4{\cdot}77 \times 10^{-18} = 0{\cdot}42 \times 10^{-18}.$$

The value of the electric moment of HCl in the normal state has been found by Frivold and Hassel * to be

$$\mu = 1{\cdot}48 \times 10^{-18}$$

from dielectric constant measurements, under the assumption that the orientation of molecules is that given by classical theory. They state that if quantum theory assumptions are used as to the orientation, the value of μ should be reduced by a factor of about $\frac{1}{2}$.

* O. E. Frivold & O. Hassel, *Phys. Zeit.* xxiv. p. 82 (1923).

It seems, however, that it may be more correct to employ the random orientation of the classical theory in interpreting their data, since the experiments were carried out at atmospheric pressure, and it seems likely that the average number of impacts per second suffered by the molecules would be large enough to more or less destroy the effects of a space quantization.

Clearly no agreement could be claimed between the above values of μ due to the nature of the problem, since the former is a measure of the absorption and depends upon the effect of a small displacement of the nuclei on the electric moment, whereas the latter represents the total electric moment of the charges in their equilibrium positions. In fact, the non-agreement of these values seems to make it certain that an accurate estimate of the absorption must be based not only upon the motion of the nuclei, but also upon the influence of this motion on the electronic configuration. The assumption as to the change of the electric moment made in §1 should accordingly be modified by saying that the change of the electric moment is proportional to the displacements of the particles relative to their centre of gravity, but that, in general, the proportionality factor may depend upon the directions of the displacements. This modification in the assumptions would have no effect upon the treatment of the absorption of diatomic molecules considered in §2, but might influence the results of the two succeeding sections to the extent that only a general agreement should be expected between the observed and calculated intensities of absorption.

I should like to take this opportunity to express my gratitude to Professor N. Bohr and Dr. H. Kramers, who have greatly aided the course of this paper both through their constant interest and through their many valuable suggestions. I also wish to express my appreciation of stipends from the International Education Board and from the University of Michigan, which have enabled me to carry on this work in Copenhagen.

Institute for Theoretical Physics,
Copenhagen.
June 9, 1925.

XIII. *The Relation between Temperature and Minimum Sparking Potential.* *By* E. F. Burton, *Ph.D., Professor of Physics, University of Toronto* *.

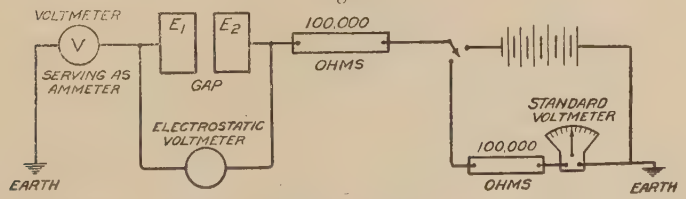
THE present investigation was undertaken to fill a gap in experimental work relating to the spark discharge in gases. The laws of spark discharge as related to variation of the gas, of pressure, of distance beween electrodes, and of material in the electrodes have been determined by many workers †. Recently Meyer ‡ and Wehrli § have determined the effect of a magnetic field on the minimum sparking potential.

As for variation in temperature, the only direct references of which the writer is aware are the experiments of Whitehead ‖ and Ryan ¶ on the variation of the dielectric strength of air with temperature. The former found that for a range from 6° C. to 41° C. the dielectric strength suffered a loss of 0·22 per cent. per degree rise in temperature.

Apparatus.

The lay-out of the apparatus is shown in fig. 1. The electrodes (E_1, E_2) were small solid cylinders of brass about 1 cm. in diameter, kept at a distance of about 4 mm.

Fig. 1.



apart inside a small quartz tube Q (see fig. 2). The electrodes were maintained in fixed position by means of the quartz nodules (*n*, *n*) and the quartz bars (B_1, B_2) pressing against the stout straight wires (*w*, *w*). The quartz tube containing the electrodes was fitted loosely into an outer glass tube (A), to which glass leading tubes were sealed in

* Communicated by the Author.

† See 'Conduction of Electricity through Gases,' Sir J. J. Thomson (Camb. Univ. Press), Chapt. xiii; F. M. Clark, Gen. Electric Review, xxviii. 3, p. 158, March 1925.

‡ E. Meyer, *Ann. d. Phys.* lviii. p. 297 (1919); lxvii. p. 1 (1922).

§ Max Wehrli, *Ann. d. Phys.* lxix. p. 285 (1922).

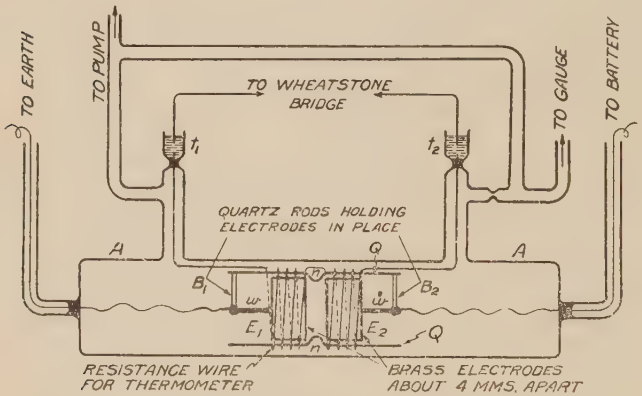
‖ Whitehead, Amer. Inst. Elec. Eng., xxix. 2, p. 1154 (1911).

¶ Ryan, Amer. Inst. Elec. Eng., p. 101 (1904).

order that the metallic connexions with the electrodes could be insulated when the whole tube A was immersed in baths at different temperatures.

In order to find whether the actual discharge had an appreciable effect on the temperature of the spark enclosure, a coil of fine nickel wire (number 34, ·05 ohm per cm.) of about 21 ohms resistance was wound about the quartz tube and connected by means of the tubes, t_1,t_2, with a Wheatstone Bridge. It was found that there was no change of any importance in the resistance of the wire when the discharge was made to pass, under the conditions of this experiment, although the resistance varied quite regularly from 8 to 40 ohms when the temperature of the nickel wire was changed from $-190°$ C. to $+200°$ C. As this fact was

Fig. 2.



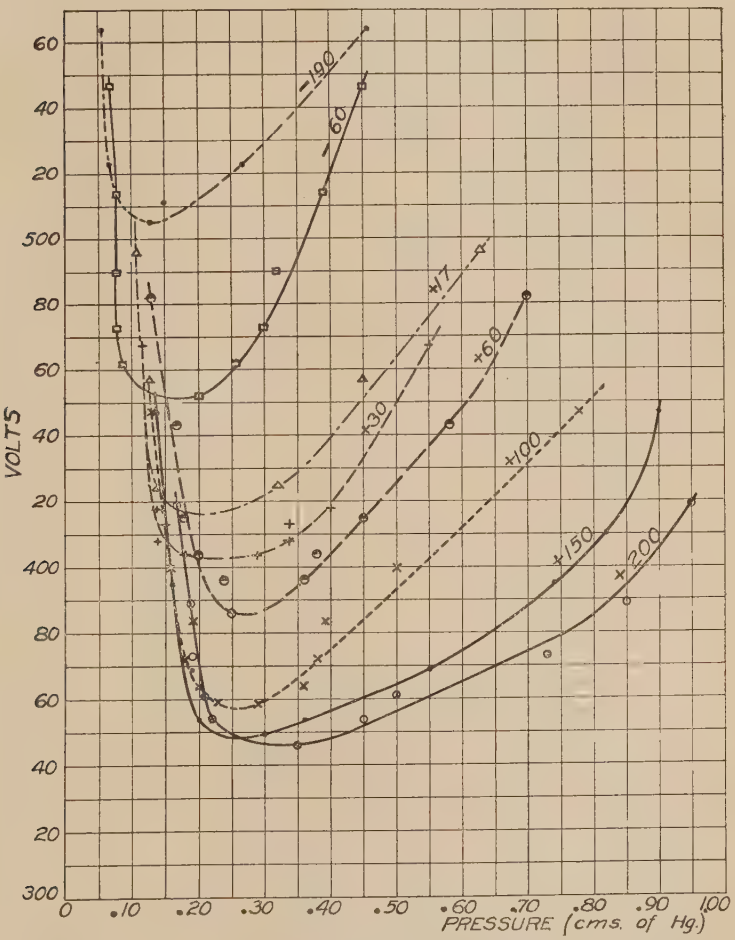
established beyond doubt, no further reference need be made to these temperature measurements. Since the nickel wire thermometer was calibrated before being sealed into the apparatus, two means of measuring the temperature of the electrodes was available, the nickel wire and an appropriate thermometer placed in the bath just outside the tube A.

In the final series of experiments the whole tube was surrounded by a copper rectangular bath (32 cm. × 8 cm. × 5 cm.), which was provided with an outer sheath of wire for electrical heating and an inner coil of copper tubing through which liquid air could be blown. For temperatures above zero, glycerine was placed in the bath; for those below zero, ether was used. The temperatures chosen for experiment were $+200°$ C., $+150°$ C., $+100°$ C., $+60°$ C., $+30°$ C., $+10°$ C., $-60°$ C., and $-190°$ C.

Manipulation and Results.

The method of determining the minimum sparking potential was that first used by Fierheller *. A potential considerably higher than the minimum sparking potential was applied, gas pumped out very gradually and the

Fig. 3.



pressure noted at which the current was first indicated on the voltmeter (V), which served as a milliammeter; the pumping was then resumed and the pressure noticed at which the spark vanished. The applied potential was then

* H. S. Fierheller, Trans. Roy. Soc. Canada, iii. p. 3 (1909).

reduced step by step and the above pressure readings repeated. The readings for different temperatures are given

TABLE I.

Pressures at which Sparks Appear and Disappear at Different Voltages and Temperatures.

200° C.	Press. in cm. Hg.		150° C.	Press. in cm. Hg.	
Voltage.	Appear.	Disappear.	Voltage.	Appear.	Disappear.
419	·95	·17	447	·90	·14
389	·85	·19	410	·82	·15
373	·73	·19	395	·74	·16
361	·50	·21	369	·55	·19
354	·45	·22	354	·36	·20
346	·35	·35	350	·30	·30
100° C.			60° C.		
447	·78	·13	482	·70	·13
400	·50	·16	443	·58	·17
384	·39	·19	415	·45	·18
372	·38	·18	404	·38	·20
364	·36	·20	396	·36	·24
359	·29	·23	386	·25	·25
30° C.			17° C.		
467	·55	·12	496	·63	·11
418	·40	·14	457	·45	·13
413	·34	·15	424	·32	·14
408	·34	·14	410	No point.	
404	·29	·18			
−60° C.			−190° C.		
547	·45	·07	564	·46	·06
514	·39	·08	523	·27	·07
490	·32	·08	511	·15	·10
473	·30	·08	505	·13	·13
462	·26	·09			
452	·20	·20			

in Table I. and illustrated by the curves in fig. 3. As the applied potential approaches the minimum looked for, both the pressures at which the spark appears and disappears and the corresponding currents (as given on V) approach to limiting values, so that the minimum can be very nicely determined.

The gas used was air freed from carbon dioxide and very carefully dried over large quantities of phosphorus pentoxide. Between readings sufficient of this dry air was admitted to the apparatus to give a pressure of four or five centimetres of mercury. Whenever the apparatus was left for any length of time, as, for example, overnight, it was exhausted to a few millimetres pressure.

One might expect to have considerable variation in the minimum potential even at a given temperature, due to possible changes in the electrodes with time. However, very consistent results were obtained, day after day, for the potential at the temperature of the room. In the final series of results which are recorded above, the bath was heated up to 200° C., and a continuous series of experiments carried out down to temperature of −190° C. without any great lapse of time; one may feel justified in saying that a variation in the electrode, merely through standing for a length of time, has been eliminated.

TABLE II.

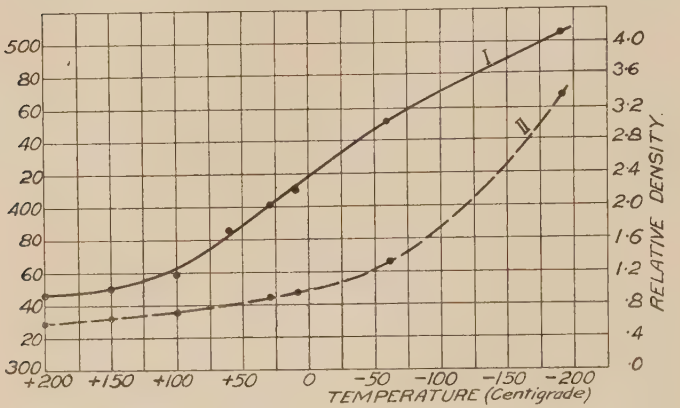
Minimum Spark Potential and Temperature.

Temperature.	Relative Density.	Minimum Potential.
200° C.	·58	346
150	·64	350
100	·73	359
60	·82	386
30	·90	402
10	·96	410
−60	1·28	452
−190	3·37 (?)	505

Table II., which is illustrated by fig. 4 (curve I), gives the collected results of the minimum spark potentials and

temperatures. These results need no comment as far as the experimental facts are concerned.

Fig. 4.



As a result of early work on minimum spark potential, it has been shown that when the distance between the electrodes is varied as well as the pressure, the spark potential depends on the mass of gas per c.c. between the electrodes.

Consequently, the relative density of the air at different temperatures was calculated, the results being recorded in Table II. and illustrated by curve II in fig. 4. In calculating the density, the variations given by Charles' law were used; as shown by the experiments of Witkowski*, the departure of air from the simple law from 100° C. to −145° C. is very small. The two curves of fig. 4 show a striking parallelism between the variation in the minimum potential of the spark discharge and the density.

I desire to express my thanks to Professor McLennan, Director of the Department of Physics, University of Toronto, for facilities offered in the cryogenic laboratory.

* A. W. Witkowski, Phil. Mag. 5, xli. p. 288 (1896).

XIV. *The Non-Metallic Elements. Connexions between their Dielectric and other Physical Properties.*—Part II. *By* G. L. Addenbrooke *.

IN a previous communication (Phil. Mag. May 1924, p. 945) relations were shown between the dielectric properties of ten non-metallic elements and their thermal properties, and also with surface tension and capillarity. The close further connexion of the electrical with the corresponding optical properties was also alluded to in general terms.

The much more direct connexion of all these properties with electrical attraction than with the dielectric constant establishes a basis for comparing the electrical with the corresponding optical properties. Such comparisons are important, as it has long been recognized that the optical properties are closely related to atomic weight, valency, chemical action, and the deeper structural properties of matter, and thus the connexion of these with the purely electrical properties is made clearer. The connexion of the optical properties with the other physical properties dealt with in the first communication is also emphasized.

In the above communication the electrical properties of the elementary gases in the *liquid state* were dealt with. It is now proposed, as a commencement, to apply similar methods and reasoning to some of the elements in the *gaseous state*, as compared with the liquid and solid states.

Table VII.

Gases.

(For data, see tables, French Physical Society, 1913.)

Property.	Hydrogen.	Helium.	Oxygen.	Nitrogen.
K	1·000,273	1·000,140	1·000,543	1·000,581
N^2	1·000,272	1·000,066	1·000,539	1·000,584

According to Avogadro's law, at the same pressure and temperature all these gases contain the same number of molecules. Since the molecules are a long distance apart, the action of the electric field must be directly on the molecules. It will be seen that K and N^2 are equal within probable errors of observation. The ordinary and atomic

* Communicated by the Author.

dielectric constants and equivalents $(K_m - 1)$ are therefore the same for these gases.

As they stand, the figures are almost meaningless; t taking the corresponding dielectric equivalents or $(K_m - 1)$ of these gases as defined in the above communication, they are closely in the proportion of :—

Helium	2	or 0·50
Hydrogen	4	„ 1·00
Oxygen	8	„ 2·00
Nitrogen.....	8·5	„ 2·12

The above relations were originally pointed out by Cuthbertson for the refractivities. For these refractivities $N^2 = K$ within the probable errors of observation. For these small dielectric equivalents or refractivities the relative results will therefore be closely similar, whether the formula $K - 1$ or $\frac{K-1}{K+2}$ is used, or the equivalent optical formulæ $N^2 - 1$ and $\frac{N^2-1}{N^2+2}$. Consequently the electrical results show that for these gases the energy stored in an electrical field is closely proportional to the attraction, and the equal correspondences in the case of the optical results imply a similar connexion at the frequencies of light waves.

Liquid State.

Consider next the liquid state of these elements when their molecules are brought six to ten times nearer each other than in the gaseous state, which is what occurs when the gases are liquified.

The data given in the table below for the densities, dielectric equivalents, and refractive indices[2] are those for the same temperature and density in the case of each element.

TABLE VIII.

Liquid State.

Element.	A.N.	A.W.	Density.	D.C.	N^2.	N^2-1.
Helium	2	4	0·15	—	—	—
Hydrogen	1	1	0·071	1·21	1·21	0·21
Nitrogen	7	14	0·88	1·43	1·43	0·43
Oxygen	8	16	1·25	1·465	1·480	0·48

The dielectric constants for this state again agree closely with the squares of the corresponding refractive indices. That for liquid hydrogen is taken from the refractive index, as it has not yet been measured directly. (See Science Abstracts 1200, 1914, and Phil. Mag. May 1924.)

Comparison of Absolute Electrical Properties in Gaseous, Liquid, and Solid States.

It has long been known that if the above gases are compressed, the values of the electric energy reversibly stored are given by the formula $\frac{K-1}{D}$ within small limits, over a wide range of pressure : that is, the energy storage in an electric field is proportional to the number of molecules present in a given volume ; experimental results are available up to about 200 atmospheres.

But the densities and electric data are known for these gases in the liquid state as well as in the gaseous. We can therefore find how many times a centimetre of each element expands from the liquid to the gaseous state at 0° C. As then the number of molecules present in a given volume will be reduced in proportion to the expansion, we can compare the electrical action on a molecule in the gaseous state with that on a molecule when the molecules are aggregated in the liquid state, and when their distance from each other is reduced from six to ten times. The comparisons are made below.

TABLE IX.

Comparison of Dielectric Equivalents of Gases in Liquid and Gaseous States.

Hydrogen Liquid.—One gramme liquid, density 0·071, occupies 14·1 cm.^{3} and 1 gramme gas at the atmospheric pressure and 0° C. fills 11,200 cm.^{3} ; thus from liquid to gas at 0° C hydrogen expands :—

$$\frac{11,200}{14\cdot1} = 975 \text{ times.}$$

K − 1 of liquid hydrogen is 0·21 and 0·21 divided by 975 = 0·000263.

K − 1 at atmospheric pressure and 0° C. is, by observation, 0·000273.

In the above it is assumed that $K = N^2$.

Oxygen.—From the liquid state at $-186°$ to A.P. at 0° C. oxygen expands 875 times.

$K-1=0{\cdot}465$, this divided by $875=0{\cdot}000530$.

The dielectric equivalent of the gas by observation at A.P at 0° C. $=0{\cdot}000543$.

Both the above are from direct observation.

Nitrogen.—The expansion of this gas is about 700 times from the liquid state at $-200°$ Density $=0{\cdot}88$. Taking $K-1$ as 0·45, this divided by 700 gives 0·000643.

The dielectric equivalent of the gas is, by observation, 0·000581.

In this case the data are a little more uncertain, but both the results are from direct observation.

Observations.

In the above examples the densities of oxygen and nitrogen at about $-190°$ are employed, and for hydrogen, $-252°$. From other data available it appears that by subtraction of more heat a further shrinkage takes place in these liquid gases as the temperature is lowered up to 10 per cent. or more by volume, but the dielectric constants are not yet available for these lower temperatures and greater densities.

Bringing the molecules still nearer would probably result in an increase of the dielectric equivalent beyond the corresponding increase in density; it may be assumed, however, that it would be small for the reasons given above.

If liquid gases of these increased densities were used the volume expansion would be correspondingly greater and thus the calculations above would not seriously be affected.

The above data, therefore, show that there is, to a close approximation, little change, not only in the relative values, but also in the atomic values of the energy stored and the corresponding attractions for a given number of atoms of these gases in an electric field of the same slope, for the gaseous and for the liquid state.

Apart from its intrinsic interest and as relating to elements so important and universal, this result supplies a basis for studying the atomic values of the actions in the other elements in the gaseous as compared with the liquid or solid states, since we can start from the same quantitative basis for both states

Similar relations for the refractivities in the liquid as compared with the gaseous state were long ago pointed out by Liveing and Dewar, though their work seems to have been overlooked. As N^2 is so close to the value of K,

both for the liquid and gaseous states, it is now obvious that the above comparison applies equally to the refractivities as to the dielectric equivalents (K − 1).

These gases are only aggregated by extreme cold as well as pressure. Also (apart from helium), these gases have the lowest dielectric equivalents and attractions of any of the elements. It is, therefore, only to be expected that the interaction between their molecules in whatever state should be small.

Extension of above Results to other Elements.

The dielectric constant of chlorine in the gaseous state is not known, nor are those of the rest of the elements we are dealing with in the state of vapour.

Owing to the long and beautiful work of Cuthbertson (Trans. Roy. Soc. 1902–1913), we have, however, the refractivities of all the elements dealt with, in the gaseous or the vapour states, reduced to 0° C. and 760 mm. pressure, as well as those of a number of others. We can, therefore, get the values of N^2-1 and $\frac{N^2-1}{N^2+2}$ for all these elements in the gaseous state from Cuthbertson's data.

Suppose we write R for N^2-1, then $\frac{N^2-1}{N^2+2}$ can be written $\frac{R}{R+3}$. Now, as R is exceedingly small for all the gaseous refractivities, the actual values of $\frac{R}{R+3}$ will in all cases be one-third those of R, to a close approximation.

Discussion of Electrical and Optical Formulæ.

The work of Boltzmann, and later of Thornton, has shown *experimentally* that in ordinary electric fields the formula $\frac{K-1}{K+2}$ represents with closeness the relation of the attraction to energy stored, for values of K from 2 to 11, or for the values of the dielectric equivalent, or energy stored in the atoms of the dielectric itself (K − 1) of from 1 to 10. Below this value of K − 1 similar evidence could only be got from experiments on gases in the liquid state. The use of the formula for values of K − 1 of less than 1 rests therefore, so far, on a theoretical basis, although reasoning offers no suggestion that it should not fairly represent the same

relations for lower values than 1 of $K-1$, or of the energy stored in dielectrics themselves, apart from that stored in the field.

On the other hand, the formula $\frac{N^2-1}{N^2+2}$ has been chiefly used by optical workers for small refractivities, where general experience has led to great reliance on it. For large ranges optical workers seem to have been chary in the past about drawing serious inferences from it; except in the cases in which K still equals N^2, there has apparently been no alternative method of co-ordination, or of experimentally checking the results, as there is in the corresponding electrical case.

The facts enumerated above, however, connect K and N^2 very closely for low values, and, as pointed out above, values of K found by the attraction method, using the formula $\frac{K-1}{K+2}$, agree closely with those found by more ordinary electric methods over a larger range than we are dealing with here, while the connexion of K and N^2 still remains intimate up to high values.

The implication is therefore very strong that as $\frac{K-1}{K+2}$ represents attraction in the purely electrical case, $\frac{N^2-1}{N^2+2}$ must be very closely connected with attraction also, for electromagnetic waves of the frequency of heat and light.

From what we know of the rapidity with which electric fields are propagated there is nothing to show that electric fields do not act similarly at the frequencies of electromagnetic waves of light.

Finally, $N-1$ is the value measured by the refractometer or spectroscope. An electromagnetic wave has frequency and amplitude, and energy depending on the first two quantities. If it is taken that $N-1$ depends on frequency and amplitude, the corresponding energy should be related at a given frequency to the square of the amplitude, and to N^2-1.

A close relation of this kind is the basis of the theories of Planck and Bohr.

It may therefore be taken that at any rate in cases where K and N^2 are found to substantially agree, there is warrant for presuming a close connexion between the attractive forces at the frequencies of light and the energy stored, under the action of these forces, and that the connexion of

the two is fairly expressed by the formula $\frac{N^2-1}{N^2+2}$, as that between attraction and energy stored is by $\frac{K-1}{K+2}$ for ordinary electric fields; the two formulæ being connected by the fact that $K = N^2$ substantially for all the elements with which we are dealing.

Application to Available Data.

Below is a table in which are collected the observational data, both optical and electrical, for all the elements we are dealing with. The gaseous optical data have been kindly supplied by Mr. Cuthbertson. The only observations as regards these are that there is an absorption band in the iodine refractivity, and almost certainly a considerable reduction would result from a proper correction applied to the figure given. Such a correction is applied in the case of selenium, which was carefully investigated by R. W. Wood (see Phil. Mag. 1902).

TABLE X.

Dielectric and Optical Properties of Elements.

Element.	Atomic Weight.	Squares of Refractive Index.		Dielectric Constants.		Densities.
		State of Elements.		State of Elements.		
		Gaseous.	Liquid or Solid.	Gaseous.	Liquid or Solid.	Liquid or Solid.
Helium	4	1·000,144	—	1·000,144	—	—
Hydrogen ...	1	1·000,272	1·21 D line	1·000,275	1·21 from N^2	0·071
Nitrogen	14	1·000,584	1·45 b	1·000,581	1·45	0·88 at −20°
Oxygen	16	1·000,539	1·46 b	1·000,543	1·47	1·25 at −19°
Chlorine	35·5	1·001,540	1·88 D line	—	1·97	1·5
Bromine	80	1·002,300	2·75 „	—	3·10	3·2
Iodine	127	1·003,840	3·70 „	—	4	4·66
Phosphorus..	31	1·002,430	4·14 „	—	3·85	1·84
Sulphur	32	1·002,220	4 „	—	4	2
Selenium	79	1·003,130	6·04 A line corrected	—	6·14	4·28
Diamond.....	12	1·000,750?	5·7 D line	—	5·5	3·5

Taking then the above data, these are analysed in Table XI.

TABLE XI.

Relative Values of Electrical and Optical Actions.

Element.	*a.* Gaseous or Vapour State. (1) N_m^2-1	*a.* Gaseous or Vapour State. (2) K_m+1	*b.* Liquid or Solid States. (1) N_m^2-1	*b.* Liquid or Solid States. (2) K_m-1	*c.* Gaseous or Vapour State. (1) $\frac{N_m^2-1}{N_m^2+2}$	*c.* Gaseous or Vapour State. (2) $\frac{K_m-1}{K_m+2}$	*d.* Liquid or Solid State. (1) $\frac{N_m^2-1}{N_m^2+2}$	*d.* Liquid or Solid State. (2) $\frac{K_m-1}{K_m+1}$
Helium	·50	—	—	—	·25	·25	—	—
Hydrogen ...	1·0	1·0	1·0	1·0	1·0	1·0	1·0	1·0
Nitrogen	2·15	2·15	2·12	2·04	2·15	2·15	2·15	2·15
Oxygen	1·94	1·94	2·0	2·02	1·94	1·94	1·94	·94
Chlorine	5·57	Data wanting, but $K=N^2$ for liquid and solid states.	6·8	7·7	5·57	Data wanting, but $N=K^2$ in all cases for liquid or solid states.	5·6	6·1
Bromine	8·02		15·0	17·8	8·02		9·75	10·5
Iodine	14·2		25	27·7	14·2		12·4	13·3
Phosphorus...	8·55		17·3	10·2	8·55		10·9	10·1
Sulphur	7·7		16·2	16·2	7·7		10·1	10·1
Selenium.....	11·26		32·0	32·2	11·26		14·2	14·25
Carbon	—		5·3	5·2	—		4·6	4·5

The figures otherwise for the liquid and solid refractivities are left as they stand : in most cases any correction would be small. A somewhat larger correction is probably required for bromine and phosphorus, but since Cauchy's formula is inadequate, a special study of each of these elements on the lines of R. W. Wood's work on selenium would be required to get the true figures, and no such investigation seems to have been made in these cases.

The differences, however, are not likely to be great enough to alter the general conclusions which a further study of the relations reveals.

Beginning with the gaseous state, as already pointed out, according to Avogadro's law, all these gases will have equal numbers of molecules in a given volume. Consequently the data show the relative atomic as well as the absolute values. If then we take the value of hydrogen as unity and divide the other values by this, we shall get a set of relative atomic values as compared with that of hydrogen. This has been done for the columns *a* and *c* in Table XI. covering the gaseous state. It will be seen that the gaseous

electrical data for seven of the elements are wanting; but we have the facts that $K = N^2$ for the three gases for which we have data, and that where data are wanting, K still equals N^2 for the liquid and solid states of the same elements.

The columns of relative values for $N_m^2 - 1$ for the liquid and solid states are calculated exactly as those for $K_m - 1$ in the first communication where the procedure was fully explained.

The columns for $\frac{N_m^2 - 1}{N_m^2 + 2}$ are again calculated from those for $N_m^2 - 1$ as before, for $\frac{K_m - 1}{K_m + 2}$. The columns for $K_m - 1$ and $\frac{K_m - 1}{K_m + 2}$ for the liquid and solid states are taken from the first communication.

We now come to the relation of the gaseous values of both kinds to those for the liquid and solid states. It was shown above that the values for the same number of atoms for the elementary gases are substantially the same for both states, and that hydrogen expands 795 times between the liquid and gaseous states. If then the actual atomic values for the liquid and solid elements are all divided by 795, we get comparative tables of the atomic values for both states, and these will correspond to the relative values given in the table, the substantially constant values of hydrogen and oxygen for both states being taken in all cases as the basis.

Consideration of above Data.

If now these four groups of tables are inspected it will be seen that:—

(1) *For the Gaseous State.*—The values of $N^2 - 1$ are the same as those for $K - 1$ as far as they are available, within errors of observation. And this applies also to the similar values of $\frac{N_m^2 - 1}{N_m^2 + 2}$ and if these are multiplied by 3, as explained above, the values all being very small.

(2) *For the Liquid and Solid States.*—Values of $\frac{N_m^2 - 1}{N_m^2 + 2}$ and $\frac{K_m - 1}{K_m + 2}$. These values seem to be generally fractionally larger for the liquid and solid states than for the gaseous,

but otherwise they are again close to the values for the gaseous state.

(3) *For the Liquid and Solid States.*—Values of N_m^2-1 and K_m-1. When these two sets of relative values are compared they are again found to be very similar to each other. While, however, the values are again very similar to those in the other tables for the elementary gases, it will be noted that, as we come to elements with higher values of N^2 and K, *the proportionate values steadily increase as compared with the values of* $\frac{N_m^2-1}{N_m^2+2}$ *and* $\frac{K_m-1}{K_m+2}$ *for both states.* Finally, for selenium (the element of highest atomic weight, attraction, and value for K), the relative values are more than twice those for $\frac{N_m^2-1}{N_m^2+2}$ and $\frac{K_m-1}{K_m+2}$. That is, the ratio of the value of energy stored to attraction is in the liquid state more than double that in the gaseous state. The atomic value for hydrogen, which is the same for both states, being taken as unity in both cases.

Alternative method of establishing the above relations.

The densities of all the above elements are known for the solid or liquid and for the gaseous states. In the latter state all will have the same number of molecules per cm.^{3} at N.P.T. The volume contractions from the gaseous to the liquid or solid state can therefore be found.

These are entered in column (*a*) in the following table :—

Table XII.

	a.	*b.*	*c.*	*d.*
Element.	Times expansion Liquid or Solid to Vapour at N. T. P.	A (N^2-1) Gaseous (*a*) as above.	Liquid or Solid (N^2-1).	Values of (*c*) taking (*b*) as unity.
Hydrogen ...	975	·265	·273	1·04
Nitrogen	700	·41	·43	1·06
Oxygen	875	·48	·48	1·02
Chlorine	475	·73	·88	1·2
Bromine	448	1·03	1·75	1·72
Iodine	410	1·57	2·70	1·72
Phosphorus	6 0	1·60	3·14	1·96
Sulphur	700	1·55	3·0	1·94
Selenium.....	605	1·90	5·04	2·65

Column (*b*) contains the refractivity^2 multiplied by the

number of times the gas contracts to the liquid or solid state. The resulting values give the refractivity^2 supposing there were no change in the atomic refractivity^2 between the two states.

Column (*c*) gives the actual refractivity^2 (N^2-1) found by observation for the liquid or solid state.

Column (*d*) gives the ratio of the gaseous atomic refractivity^2 on the above basis to that actually found for the liquid and solid states. It will be seen that for the three noble gases the differences are small, as already pointed out. As, however, the dielectric equivalents and refractivities of the elements increase, and presumably the attractions of their atoms for each other, the differences become greater and finally more than double. These differences rise with increasing atomic weight or number, and also with position in the periodic table. The only apparent cause is the difference in aggregation.

It is noteworthy that the increasing differences also correspond with increasing differences in viscosity or hardness.

For the three noble gases Maxwell's law is closely obeyed for both states. Assume that if the dielectric equivalents ($K-1$) for the vapours of the rest of the elements were found they would also accord with Maxwell's relation to the already known refractivities, as seems highly probable. Then we should have Maxwell's law obeyed to a close approximation for all these elements for both states.

But the atomic values would be different in the above proportions for the two states. Consequently we should have the refractivity and the dielectric equivalent for these elements varying through a considerable range in close agreement with each other. In considering the constitution of non-metallic matter it seems equally important to ascertain if possible whether the above deduction is correct, or, if incorrect, what are the real relations.

Experimenters in the past have been deterred from attempting to obtain these dielectric constants for various reasons, but recent experience of the writer's with liquid bromine, specially purified and dried by Professor H. B. Baker, shows that this can be kept for several weeks in the presence of large platinum surfaces without any action taking place. Prof. Baker has also shown that chlorine gas, highly dried, will not unite with equally dried hydrogen, even in sunlight.

Pending such final verification, we have the evidence adduced above, which seems almost conclusive and which

shows that the property of occluding energy (reversibly) in a given electric field is only a constant under clearly defined circumstances. It is a pity a better descriptive phrase than "the dielectric constant" cannot be found for this important and fundamental property of matter, and for the even more direct quantity (K—1), which I have ventured to call the dielectric equivalent, or the equivalent of the energy stored in the dielectric itself.

The Real Nature of Faraday's "Specific Inductive Capacity," called more lately, "The Dielectric Constant."

Briefly, the property of matter called at present "the dielectric constant" is really an unfortunate name for the proportional amount of energy stored between the electrodes of a condenser and the field, plus that stored in a dielectric filling the space between them, in terms of the former.

When the energy stored between the electrodes is deducted and that only considered which is stored reversibly in the dielectric itself, it is evidently dependent for the non-metallic elements on the following factors :—

(1) Position in the periodic table. That is on the form of the arrangement of the electrons round the nucleus of each of the atoms of the dielectric.

(2) On the charges of the nucleus and of the corresponding number of electrons surrounding it in each atom. That is, for the dielectric elements in any given columns in the periodic table, K—1 increases with the atomic number and weight, apparently nearly directly.

(3) On the aggregation of the atoms. For a given aggregation of atoms it is greater the higher the atomic value of (K—1) as defined above. Therefore, in gases having small attraction, the increase is small, but grows greater in elements where the atomic attractions are greater and the aggregations denser. The larger changes occur where atoms of higher atomic numbers condense from a gaseous to a liquid or solid state.

Using the broad lines of the modern view of the character of atomic structure, it is easy to form a fairly comprehensive picture mentally of what occurs to dielectric matter when placed in ordinary electric fields.

This is especially the case if the views of the nature of ordinary electric absorption, mentioned later, are also adopted.

We have then a useful background for considering what takes place in dielectrics when absorption is present in addition to the fundamental action, which should form a foundation on which to develop sound views of the construction of non-metallic matter.

Supplementary Evidence.

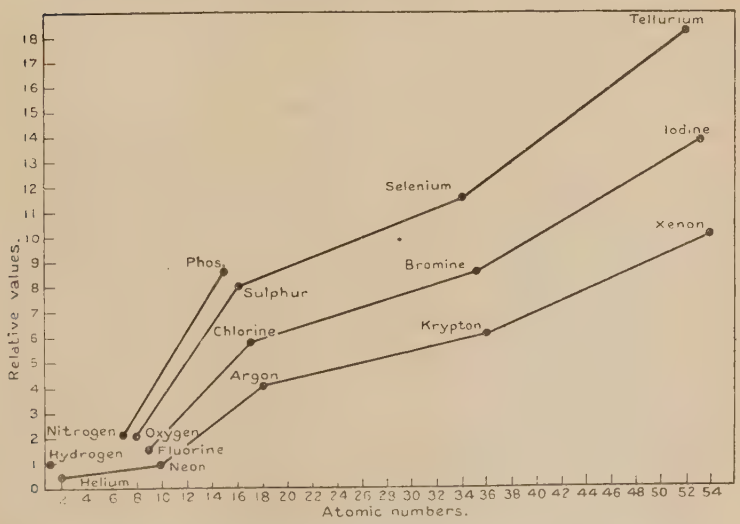
It has already been mentioned that Cuthbertson has found the gaseous refractivities for a number of other elements besides the ten or eleven with which we have been dealing. In view of the intimate connexion shown above between the purely electrical and the so-called optical properties of elements, for which we have the data for both properties, it is of interest to embody these further data in a diagram. This will include the data for the rare gases and also for gaseous tellurium and fluorine.

As these gaseous refractivities are very small, $N-1$ will practically be equal to $\frac{N^2-1}{2}$, and to $\frac{N^2-1}{N^2+2} \times \frac{3}{2}$ in all cases within the limits of accuracy to which we need go. Thus the relative values of all these properties can be represented by one set of relative values, if we take that of hydrogen as that of unity in each case.

Gaseous State.

Relative values of (2) N^2-1 and (1) $\frac{N^2-1}{N^2+2}$ (atomic), and thus presumably of

(1) Electric attraction between molecules.
(2) Electric storage capacity (atomic).



In the above diagram the abscissæ are atomic numbers and the ordinates the relative values of the above quantities, taking that of hydrogen as unity in all cases.

The orderly way in which the various elements group themselves step by step in accordance with their position in the periodic table is very striking, as well as the very defined steps by which the properties progress from one group to the next higher. There is an evident sameness in the influence underlying the changes which occur between one group and the next. If we can connect these properties with the attractions due to electromagnetic waves impinging on the atoms and the corresponding amount of energy momentarily occluded in them, the connexions seem still more significant.

Connexion with Ordinary Electrical Properties.

Finally, it was shown above that the properties of the elementary gases, hydrogen, oxygen, and nitrogen, are substantially the same atomically in the liquid as well as in the gaseous state. If then the relative gaseous values are taken for N^2-1 or the corresponding capacity for storing electric energy, and these relative values are multiplied by 975 for the elements below oxygen, it will be found that lower values result than the corresponding values for N^2-1 and $K-1$ in the liquid or solid states. This again points to the view that the difference in capacity for storing electric energy in an electric field between the gaseous and liquid and solid states is due to aggregation of the atoms in the latter states. On the other hand, the values for the attractions (atomic) for both states accord fairly, so that while their values are only slightly modified by the state of aggregation of the atom, the energy stored due to this attraction is seriously increased with greater aggregation which also increases with atomic weight and position in the periodic table

As regards boron, carbon, and silicon, reliable data for the gaseous state do not appear to exist at present, nor for boron and silicon in the solid state. If the electrical and optical data for these three elements could be found, the properties of the whole or of the non-metallic elements would be much better defined over an enormous range of wave-lengths.

A moderate effort and financial expenditure, with some goodwill and organization, should enable all the above optical data to be checked and corrected for long waves, and the corresponding electrical data to be found. If such data were available, the results could hardly fail to help considerably in connecting our knowledge of the properties of atoms by themselves with those of the same atoms forming matter in the aggregate.

Basis of above Comparisons.

Although in these two communications the modern atomic theory has been freely used for purposes of illustration as undoubtedly giving much the most plausible explanations of the phenomena, it is worthy of note that none of the results depend on this theory.

Boltzmann showed experimentally, in 1873, that the ratio of the attraction of a dielectric to a metal sphere in an electric field could be expressed in terms of $K-1$, as $\frac{(K-1)}{(K-1)+3}$, or $\frac{K-1}{K+2}$, and his work was extended to a greater range of dielectrics by Thornton in 1908. Maxwell's relation was first put forward in 1865, and the corresponding optical formula $\frac{N^2-1}{N^2+2}$ was advanced by the two Lorentz in 1890. It is probable, therefore, that all the relations described above would have been discovered by this time, even if there had been no more detailed knowledge of the nature of the atom than there was in Maxwell's time.

Effects of Aggregation on Atoms.

Sir J. J. Thomson has for many years been pointing out that, in the case of a solution, the attraction (roughly defined by the dielectric constant) of the atoms of the solvent will loosen the bonds or lines of force binding the atoms of the molecules of the solute, and will exercise a powerful influence in causing the disruption of its molecules into ions.

But there is no difference in principle between the atoms of a solvent and a solute; they are equally made up of opposite electric charges. If, then, the atoms of a solvent act on those of a solute, as Sir J. J. Thomson has pointed out, it seems to follow that there must be a similar action between the atoms of the solvent itself tending to loosen the tension between the nuclei and surrounding electrons as compared with the same atoms in the gaseous state, thus making the whole aggregation more elastic.

Again, if an aggregation of atoms attract each other, and so loosen the bonds between the nuclei and their surrounding electrons, it seems to follow that if such an aggregation of atoms is put in an electric field some more of the lines which formerly anchored between the nuclei and the electrons will be diverted to the field, and so there will be a further

loosening or diversion of lines of force between the nuclei and electrons, and this may increase further the elasticity of of the whole aggregation and cause a very small but visible expansion.

Such an action might account for "Electrostriction." Quincke formed a leyden-jar of a thermometer bulb with the glass as the dielectric; on charging strongly the liquid in the stem sinks, that is, the glass expands.

If the above reasoning has solid basis, it seems possible to account in these ways for what is found to occur experimentally in good dielectrics in electric fields.

Nature of Absorption, Electrical and Optical.

The so-called "resistance" of dielectrics is practically another name for absorption, and where the resistance is high, absorption is comparatively small. Where this latter is the case, measurements of capacity made with alternating currents of fair frequency give a close approximation of the true, or, as it has been called, the instantaneous or geometrical capacity, or the true capacity of the atoms of the dielectric itself when the capacity of the field itself is deducted.

Experiments on and investigation of the resistances of the dielectric elements in these communications led to the conclusion that for all the elements dealt with here the resistances were high enough to warrant the conclusion that the capacities and dielectric properties were sufficiently near the true ones to make legitimate the uses to which the have been put.

The value of the relationships found between the electrical and other physical properties of the elements would, however, be greatly enhanced if they could be followed up and applied to compounds formed from these different elements, but in these cases absorption may often be present.

If absorption in the general run of dielectrics at ordinary frequencies was part of the action of the field on the individual atoms of dielectrics, as has often been assumed in the past, the actions of ordinary electric fields on matter would, outside the best dielectrics, be very complicated and confusing.

Optical absorption, of course, rests on a different basis; this, which is generally of an atomic character, does not appear to come in until the frequencies of heat and light are approached.

The writer's experience, however, has led to the conclusion that ordinary electric absorption when seriously present is due, not to an action on the mass of the molecules of a

dielectric, but to action on small percentages of electrolytic impurities dissolved in the dielectric, which either wholly or in part are in an ionized state, as they would be in an electrolytic solution. (See Journal Electrical Engineers, February 1919, under "Institution Notes," also a long letter to 'Nature,' April 5th, 1924.)

The writer has recently found that similar views on absorption in almost similar terms were put forward by P. Curie in two lectures which he gave to the French Physical Society in 1892, as the result of work by his brother, J. Curie, and himself. They derived their conclusions chiefly from work on crystals. It is unfortunate that the lectures seem only to have been published in epitome. That such distinguished and far-seeing experimenters as the Curies should have arrived at almost precisely similar conclusions to the writer, on evidence derived from experiments of an entirely different character and by entirely different methods, encourages the writer to put forward more definitely the conclusions to which he has been led. Correct views of dielectric absorption are of great importance, not merely as a technical question, but in the study of physics and chemistry, and even in elucidating the nature and properties of matter itself.

These questions cannot be further discussed here, but it may be pointed out that what has been said above leads broadly to the view that there is no fundamental difference between what are called dielectrics and ordinary electrolytic solutions of all kinds ; the apparent differences depend on the amount of ions present usually of a second substance, and the nature of the contact between the solvent and the electrodes and the liquidity or solidity of the matter through which the ions are diffused. In all these cases it would appear that the mass of matter forming the bulk of the substance is inert in electric fields, except for the attractions and reversible storage of energy taking place as described above. Electrolytic actions and the actions studied under the term "absorption" arise from the action of the field on the more or less free ions in electrolytes and more or less confined ions in dielectrics. It is to action on these ions and their consequent movements that changes of capacity with changes of frequency and temperature are due, as well as the dissipation of energy which is always found to occur concurrently, and which is usually studied as resistance or conductivity or dielectric hysteresis. Very small percentages of moisture or other electrolyte in dielectrics are found experimentally to have considerable effects.

Up to the end of last century there were no methods available for separating the capacity effects and dissipation of energy due to absorption in electric fields from the fundamental or instantaneous capacity, and much confusion of ideas resulted, and still exists.

By the use of the electrostatic wattmeter or by alternating bridge measurement, both of which methods have been greatly perfected during the last few years, it is now possible, at any rate in alternating fields, to separate the energy dissipated in dielectrics from that reversibly stored or from the capacity action. Further, by measurements over a range of frequencies, especially if very low frequencies are also used, change of capacity with change of frequency can also be measured. This change of capacity with change of frequency and the accompanying dissipation of energy, the writer's experiments show to be due to the presence of ions, the true instantaneous capacity being unaffected by change of frequency within ordinary limits. The very remarkable temperature coefficients of dielectrics are also found by experiments to be due to the presence of electrolytic ions and not to action on the mass of the molecules of dielectrics, the true temperature coefficients of which latter are, as those of the refractive index, always nominal.

In the above, and other ways, it is possible now to separate absorption effects, including both capacity and dissipation of energy, from the true basis capacity action to a fair approximation, and thus to arrive at a much closer idea of the real nature of the actions of dielectrics in electric fields and the real properties of matter.

Unfortunately, these methods have so far been applied to comparatively few dielectrics, but, from the writer's experience, if they were applied to the dielectrics in the long lists of dielectric constants given in the leading tables of physical constants, there would be considerable alteration in numbers of cases. This is the chief difficulty in pursuing the subject further at present. There is the same difficulty in applying much present data to problems in physical chemistry, as is now being done. False or incorrect inferences are being drawn, but if true data were available valuable light would be thrown on some of these problems.

Again, if the views expressed above are correct, we have a valuable means of studying absorption and electrolytic action by themselves.

It has only been possible to deal with the subject very cursorily, and it is difficult to avoid being misunderstood without writing at much greater length, but the object of

these two communications will have been attained if what has been said draws attention to the vast field for further experiment on recognized lines which is open in these directions, and which, if explored further, would certainly do much to extend and clarify our ideas of the physical actions which go to make up the properties of matter in the aggregate.

XV. *On an Experimental Investigation of the Applicability of Saint-Venant's Principle to the case of Frameworks having Redundant Bracing Members.* *By* Prof. A. J. Sutton Pippard, *M.B.E., D.Sc., University College, Cardiff, and* G. H. W. Clifford, *M.Sc.* *

A RECENT paper † records an experimental verification of Castigliano's Principle of Least Work, and at the suggestion of Prof. Horace Lamb, F.R.S., the structural model and methods of strain measurement described therein were used to investigate the applicability to the case of redundant frameworks of Saint-Venant's Principle of the elastic equivalence of statically equipollent systems of load.

This principle states that the strains which are produced in a body by the application to a small portion of its surface of a system of forces statically equivalent to zero force and zero couple, are of negligible magnitude at distances which are large compared with the linear dimensions of the part ‡.

Saint-Venant gave no formal proof of this principle, which was enunciated with reference to elastic solids, but experimental evidence shows that the strains due to such a system become negligible at a comparatively short distance from the point of application of the forces §.

During the progress of an investigation into the distribution of stresses in the hull of a rigid airship ‖, it appeared probable that the scope of the principle could be extended to the case of a framework having redundant bracing members, and a general demonstration of this was given by Mr. R. V. Southwell in a paper ¶ which also presented a physical basis for the principle in its usual form.

In the case of a simply stiff framework, *i. e.* one in which

* Communicated by the Authors.

† Phil. Mag. l. (July 1925).

‡ A. E. H. Love, 'Mathematical Theory of Elasticity,' 3rd ed. p. 129.

§ Cp. G. F. C. Searle, 'Experimental Elasticity,' p. 31 *et seq.*

‖ Aeronautical Research Committee R. & M. 800.

¶ Phil. Mag. xlv. (January 1923).

there are just sufficient bars to maintain the geometry of the structure, the internal stress distribution under any external load system is governed only by the configuration of the framework, and the stresses in a particular member may vary considerably under the action of load systems which are statically equivalent. It is therefore clear that the principle of Saint-Venant is not applicable to this class of framework ; it is only when the stress distribution becomes a function of the elastic properties of the framework that it can operate. This essential condition is fulfilled by a redundant structure, but since the degree of redundancy may range from a single member more than the number required for stiffness, to an infinite number in the extreme case of a solid body, it is clearly a matter of great importance to determine the effect of the number and disposition of redundancies upon the operation of the principle, and the experiments to be described were designed to contribute some information on these points.

By combining this principle with the principle of superposition, it follows that if any statically equivalent load systems be applied separately to a small portion of the surface, then the strains produced by these separate systems will tend towards the same values as the distance from the surface of application increases, and this modified form of the principle was found to be more convenient for experimental purposes than the original.

Description of Experiments.—The structure used in the experiments was the hexagonal braced tube with a $\frac{7}{8}$ in. solid keel member, described and illustrated in the previous paper *. This paper also describes the method of strain measurement.

The loads in the diagonal wire members only were measured, the longitudinal loads being obtained from these by resolution at the joints.

The framework was three bays in length, and a number of different statically equivalent load systems were applied to the bulkhead farthest from the wall and designated as bulkhead D.

Since it was desired to show if possible the effect of the disposition and number of redundancies, the experiments were divided into four sets as follows :—

Set No. 1.—All bulkheads unbraced ; all panels counterbraced.

Set No. 2.—Bulkhead D radially braced with 4 B.A. rods ; all panels counterbraced.

* Phil. Mag. l. (Experiment 3, p. 107).

Set No. 3.—Bulkheads C and D radially braced with 4 B.A. rods ; all panels counterbraced.

Set No. 4.—Bulkhead D radially braced with 4 B.A. rods ; compression counterbracing members omitted from all panels.

Fig. 1.

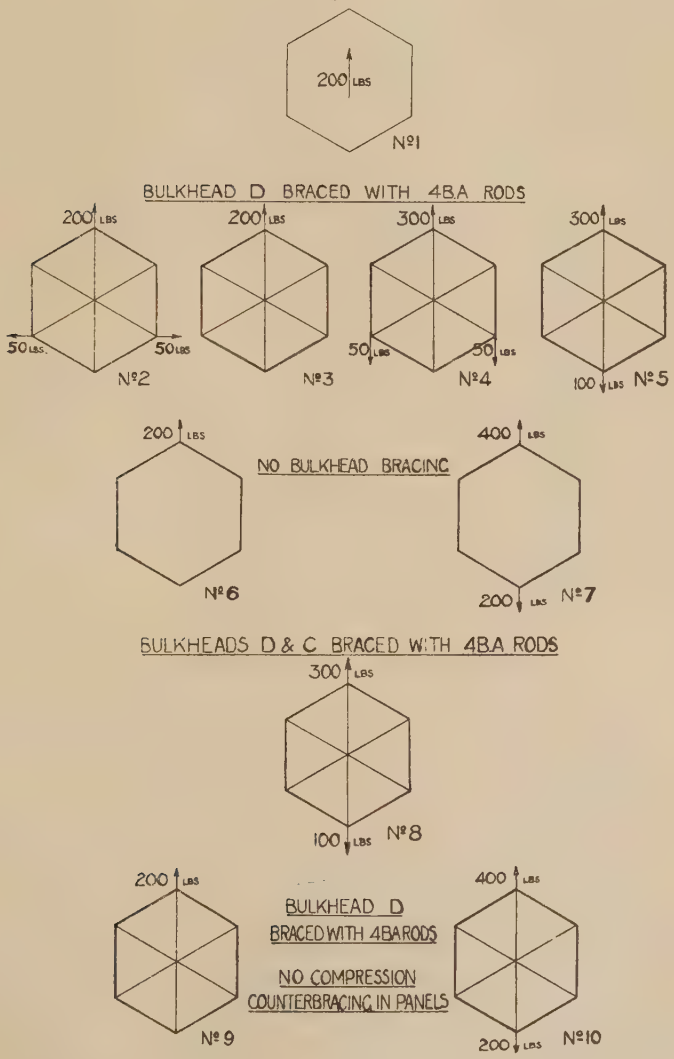


Diagram of loading and reference chart to experiments.

The scheme of the experiments and diagram of the load system is shown in fig. 1, the net shear being 200 lb. in each case.

A general theoretical solution for the stresses in a braced hexagonal tube, loaded at one end bulkhead and rigidly held at the other, has been obtained * by assuming that the loaded bulkhead is rigid in its own plane, and that all transverse struts throughout the structure are inextensible. An extension of this solution to include the effect of the elasticity of the transverse struts shows this effect to be very small.

An identical stress distribution with that given on the assumption of a rigid bulkhead can be obtained if the bulkhead be considered to be unbraced, and the net shearing force to be obtained by a particular distribution of loads among the nodes of the transverse frame.

The stress distribution obtained from the general solution can thus be used as a theoretical datum for the first three sets of experiments, and for convenience of reference it is included in fig. 1 as No. 1.

Nos. 2–5 on the diagram show the load systems adopted in Set No. 2, these being the experiments actually carried out first. The greatest variations from the theoretical case were given by No. 5, and so for Set No. 1 the loadings No. 6 and No. 7 on the diagram were taken.

For Set No. 3 only one case, (No. 8 on the diagram), was measured for comparison with No. 1.

Nos. 9 and 10 illustrate the loadings adopted for the experiments of Set No. 4.

Experimental Results.

Set No. 1. *All bulkheads unbraced*; *all panels counterbraced.*

The loads in the wires as measured, and those in the longitudinals obtained from these are given in Table I. for load systems Nos. 6 and 7 on the chart.

It is evident at once that the load applied to the top joint of the structure as in load system No. 6, tends to stress mainly the members in the top panels, and in a length of three bays very little is transmitted to the bottom panels.

This effect is also seen by comparing the loads in the top panels (3–4) for the two cases Nos. 6 and 7. In load system No. 7 there is 400 lb. at the top joint compared with 200 lb. in load system No. 6, and the stresses in the top panels are approximately doubled. These are set out again in Table II. for easy reference.

* Compare Aeronautical Research Committee R. & M. 800, Appendix V.

TABLE I.

Member.	Measured Loads.		Theoretical Loads.
	No. 6.	No. 7.	No. 1.
C_1D_1	Nil.	−228·4	33·6
C_2D_2	−2·8	85·6	17·6
C_3D_3	102·6	199·0	−11·6
C_4D_4	−211·6	−424·2	−50·6
C_1D_2	+3·6	−125·4	25·9
C_2D_1	Nil.	148·8	−21·9
C_2D_3	10·6	27·6	49·4
C_3D_2	Nil.	14·0	−49·0
C_3D_4	137·6	276·0	33·0
C_4D_3	−144·0	−286·0	−34·3
B_1C_1	+5·6	−578·4	101·2
B_2C_2	15·0	300·0	53·2
B_3C_3	263·4	530·0	−34·8
B_4C_4	−633·2	−1268·8	−152·0
B_1C_2	−5·2	−128·0	29·8
B_2C_1	Nil.	102·4	−18·0
B_2C_3	32·6	64·0	49·9
B_3C_2	−7·4	25·6	−48·4
B_3C_4	130·0	263·2	31·5
B_4C_3	−104·6	−204·4	−35·6
A_1B_1	−2·4	−918·8	168·9
A_2B_2	41·4	481·2	88·6
A_3B_3	378·8	812·0	−58·2
A_4B_4	−1001·2	−1996·2	−253·4
A_1B_2	−12·6	−132·6	33·8
A_2B_1	Nil.	93·6	−14·0
A_2B_3	62·4	104·0	50·4
A_3B_2	11·0	63·2	−48·1
A_3B_4	134·6	269·6	30·2
A_4B_3	−89·8	−181·6	−37·0

TABLE II.

Member.	Load System 6.		Load System 7.
	Load.	(Load)×2.	Load.
C_3D_3	102·6	205·2	199·0
C_4D_4	−211·6	−423·2	−424·2
C_3D_4	137·6	275·2	276·0
C_4D_3	−144·0	−288	−286·0
B_3C_3	263·4	526·8	530·0
B_4C_4	−633·2	−1266·4	−1268·8
B_3C_4	130·0	260·0	263·2
B_4C_3	−104·6	−209·2	−204·4
A_3B_3	378·8	757·6	812·0*
A_4B_4	−1001·2	−2002·4	−1998·0
A_3B_4	134·6	269·2	268·0
A_4B_3	−89·8	−179·6	−181·6

* This member shows a greater discrepancy, because it is the first to be affected appreciably by the variation in the stresses in the 2–3 panel wires.

On further comparison, the stresses in the members of the bay AB for the three load systems Nos. 6, 7, and 1, show very little tendency to converge to the same values.

It would appear, therefore, that in a framed tube in which all panels are redundantly braced, but in which there is no bracing in the plane of the applied load system, the operation of the Saint-Venant Principle, even if it exists, is a very slow process.

Set No. 2. *Bulkhead D radially braced with* 4 *B.A. rods ; all panels counterbraced.*

The various load systems applied in this case are shown in the diagram Nos. 2–5. Of these the stresses for No. 3 had

TABLE III.

Member.	Calculated Load. lb.	Measured Load. lb.			
	1.	2.	3.	4.	5.
C_1D_1	33·6	35·1	32·5	36·3	21·6
C_2D_2	17·6	18·0	19·0	15·1	27·3
C_3D_3	−11·6	−12·2	−11·8	−9·2	−8·2
C_4D_4	−50·6	−50·8	−52·0	−54·9	−63·4
C_1D_2	25·9	26·0	24·7	25·8	14·5
C_2D_1	−21·9	−22·8	−21·1	−23·6	−14·0
C_2D_3	49·4	49·7	49·6	49·6	51·0
C_3D_2	−49·0	−49·4	−49·4	−45·4	−50·0
C_3D_4	33·0	33·0	33·8	35·7	41·2
C_4D_3	−34·3	−33·8	−34·2	−37·6	−40·3
B_1C_1	101·2	102·6	98·8	101·2	65·8
B_2C_2	53·2	54·0	55·0	50·3	73·0
B_3C_3	−34·8	−35·7	−33·8	−24·4	−22·7
B_4C_4	−152·0	−149·4	−153·0	−165·8	−177·4
B_1C_2	29·8	29·9	30·3	27·3	26·5
B_2C_1	−18·0	−17·9	−18·3	−16·4	−14·2
B_2C_3	49·9	49·2	49·2	50·1	50·0
B_3C_2	−48·4	−49·9	−48·7	−47·1	−49·0
B_3C_4	31·5	31·0	31·6	34·4	33·8
B_4C_3	−35·6	−35·0	−36·3	−40·1	−40·0
A_1B_1	168·9	170·0	166·6	161·0	123·4
A_2B_2	88·6	91·0	89·7	88·7	113·2
A_3B_3	−58·2	−60·7	−57·8	−40·5	−42·0
A_4B_4	−253·4	−248·7	−255·0	−280·8	−283·8
A_1B_2	33·8	33·4	33·9	33·4	33·8
A_2B_1	−14·0	−13·9	−13·7	−11·6	−10·9
A_2B_3	50·4	49·7	51·2	48·0	50·3
A_3B_2	−48·1	−50·2	−48·2	−49·6	−50·2
A_3B_4	30·2	29·5	30·0	34·6	29·2
A_4B_3	−37·0	−36·1	−37·2	−39·8	−40·4

already been obtained in the earlier experiments *, but all the others entailed new measurements. The stresses as measured and those calculated for No. 1 are given in Table III.

To show the variation in the stresses more clearly, the differences from the theoretical case have been calculated and are given in Table IV.

TABLE IV.

Member.	No. 2.	No. .	No. 4.	No. 5.
C_1D_1	1·5	−1·1	2·7	−12·0
C_2D_2	0·4	1·4	−2·5	9·7
C_3D_3	0·6	0·2	−2·4	−3·4
C_4D_4	0·2	1·4	4·3	12·8
C_1D_2	0·1	−1·2	−0·1	−11·4
C_2D_1	0·9	−0·8	1·7	−7·9
C_2D_3	0·3	0·2	0·2	1·6
C_3D_2	0·4	0·4	−3·6	1·0
C_3D_4	0	0·8	2·7	8·2
C_4D_3	−0·5	−0·1	3·3	6·0
B_1C_1	1·4	−2·4	0	−35·4
B_2C_2	0·8	1·8	−2·9	19·8
B_3C_3	0·9	−1·0	−10·4	−12·1
B_4C_4	−2·6	1·0	13·8	25·4
B_1C_2	0·1	0·5	−2·5	−3·3
B_2C_1	−0·1	0·3	−1·6	−3·8
B_2C_3	−0·7	−0·7	0·2	0·1
B_3C_2	1·5	0·3	−1·3	0·6
B_3C_4	−0·5	0·1	2·9	2·3
B_4C_3	−0·6	0·7	4·5	4·4
A_1B_1	1·1	−2·3	−7·9	−45·5
A_2B_2	2·4	1·1	0·1	24·6
A_3B_3	2·5	−0·4	−17·7	−16·2
A_4B_4	−4·7	1·6	27·4	30·4
A_1B_2	−0·4	0·1	−0·4	0
A_2B_1	−0·1	−0·3	−2·4	−3·1
A_2B_3	−0·7	0·8	−2·4	−0·1
A_3B_2	2·1	0·1	1·5	2·1
A_3B_4	−0·7	−0·2	4·4	−1·0
A_4B_3	−0·9	0·2	2·8	3·4

In a discussion upon the accuracy of the experimental results in the first paper, it was stated that repeat readings on the wires could be made to within ±1 lb., so that it may be assumed that any variation within these limits can be neglected.

With the load system No. 2 only two wires out of eighteen measured show variations outside these limits, and in the case of load system No. 3 only one out of the eighteen exceeds 1 lb. and this only by 0·2 lb.

* Phil. Mag. I. (1925).

It may be assumed, therefore, that within the limits of experimental accuracy, the load systems Nos. 2 and 3 give stresses agreeing throughout with the theoretical case No. 1.

With the load system No. 4 the variations are larger, but corrections of $\pm$ 1 lb. to the readings have such a considerable effect that deductions from this case are inconclusive.

TABLE V.

Member.	Load.		Variation of No 5 from No. 1.	
	No. 1.	No. 5.	lb.	Per cent. of No. 1.
C_1D_1	33·6	21·6	−12	−35·7
B_1C_1	101·2	65·8	−35·4	−35·0
A_1B_1	168·9	123·4	−45·5	−27·0
C_2D_2	17·6	27·3	9·7	55·0
B_2C_2	53·2	73·0	19·8	37·2
A_2B_2	88·6	113·2	24·6	27·6
C_3D_3	−11·6	−8·2	−3·4	−29·3
B_3C_3	−34·8	−22·7	−12·1	−34·8
A_3B_3	−58·2	−42·0	−16·2	−27·8
C_4D_4	−50·6	−63·4	12·8	25·3
B_4C_4	−152·0	−177·4	25·4	16·7
A_4B_4	−253·4	−283·8	30·4	12·0
C_1D_2	25·9	14·5	−11·4	−44·0
B_1C_2	29·8	26·5	−3·3	−11·0
A_1B_2	33·8	33·8	0	0
C_2D_1	−21·9	−14·0	−7·9	−36·0
B_2C_1	−18·0	−14·2	−3·8	−21·1
A_2B_1	−14·0	−10·9	−3·1	−22·1
C_2D_3	49·4	51·0	1·6	3·2
B_2C_3	49·9	50·0	...	...
A_2B_3	50·4	50·3	...	...
C_3D_2	−49·0	−50·0	...	...
B_3C_2	−48·4	−49·0	...	...
A_3B_2	−48·1	−50·2	2·1	4·3
C_3D_4	33·0	41·2	8·2	24·8
B_3C_4	31·5	33·8	2·3	7·3
A_3B_4	30·2	29·2	...	...
C_4D_3	−34·3	−40·3	6·0	17·5
B_4C_3	−35·6	−40·0	4·4	12·3
A_4B_3	−37·0	−40·4	3·4	9·2

With load system No. 5, however, the variations from No. 1 are much more marked, and the figures obtained have therefore been selected for detailed analysis.

In Table V. the variation of the stresses from those due to load system No. 1 are given as percentages of the latter. The members are arranged in groups of three, each group consisting of the corresponding members in the three bays. Variations of 1 lb. or less are neglected.

It will be seen that there are ten groups of corresponding members, and in seven of these groups there is a progressive drop in the percentage variation of stress from the bay CD to the bay AB. In two of the remaining three groups, (the 3–3 and 2–1), the figure for the bay BC does not lie between those for the other bays, although the variation is less in AB than in CD. Corrections of less than 1 lb. to the readings of one member in each group would, however, cause these two groups to show a progressive drop.

The only remaining group (3–2) can similarly be adjusted by corrections of less than 1 lb. to the readings.

Hence, seven of the groups show a progressive diminution of percentage variation without any correction of the experimental results, while adjustments of the remaining three by amounts within the limits of experimental accuracy would cause these to show a similar progression. Of the experiments in this set, therefore, the stresses for Nos. 2 and 3 agree almost exactly with those for No. 1, while No. 5 shows that there is a distinct tendency towards the equalization of stresses when bracing is provided in the plane of the external load system.

Set No. 3. *Bulkheads C and D radially braced with* 4 *B.A. rods ; all panels counterbraced.*

Since in Set No. 2 the load system No. 5 gave the greatest variation from the theoretical case, the same loading was adopted for the present set of experiments, in which the two bulkheads C and D were radially braced.

The loads for this case are given in Table VI., together with the variation from those of No. 1 as before, variations of less than 1 lb. being neglected.

In this set of experiments the loads afford very definite evidence of the rapid equalization of stresses. In five out of the six wires in the CD bay the variation between the two systems of loading is considerable, but in the bay AB the variation has been reduced to negligible dimensions in every

TABLE VI.

Member.	Loads.		Variation from No. 1.	
	No. 1.	No. 8.	Actual.	Per cent. of No. 1.
C_1D_1	33·6	22·8	−10·8	−32·2
B_1C_1	101·2	84·2	−17·0	−16·8
A_1B_1	168·9	151·0	−17·9	−10·6
C_2D_2	17·6	16·5	−1·1	−6·2
B_2C_2	53·2	55·5	2·3	4·3
A_2B_2	88·6	90·3	1·7	1·9
C_3D_3	−11·6	+1·0	−12·6	−108·6
B_3C_3	−34·8	−4·2	−30·6	−88·0
A_3B_3	−58·2	−28·4	−29·8	−51·2
C_4D_4	−50·6	−75·7	25·1	49·5
B_4C_4	−152·0	−197·5	45·5	30·0
A_4B_4	−253·4	−297·7	44·3	17·5
C_1D_2	25·9	19·3	−6·6	−25·4
B_1C_2	29·8	30·3	...	...
A_1B_2	33·8	33·7	...	...
C_2D_1	−21·9	−14·8	−7·1	−32·4
B_2C_1	−18·0	−20·6	2·6	+14·4
A_2B_1	−14·0	−13·1	...	...
C_2D_3	49·4	47·8	−1·6	−3·2
B_2C_3	49·9	50·7	...	...
A_2B_3	50·4	50·9	...	...
C_3D_2	−49·0	−40·8	−8·2	−16·7
B_3C_2	−48·4	−48·1	...	...
A_3B_2	−48·1	−48·8	...	...
C_3D_4	33·0	49·2	16·2	49·1
B_3D_4	31·5	30·1	−1·4	−4·5
A_3B_4	30·2	29·5	...	...
C_4D_3	−34·3	−49·1	14·8	43·2
B_4C_3	−35·6	−35·6	...	...
A_4B_3	−37·0	−37·4	..	...

case, and even in the bay BC four of the six wires show negligible variation.

The introduction of an extra bulkhead bracing system has therefore caused the stress equalization to take place much more quickly than is indicated by the results of the experiments of Set No. 2.

Set No. 4. Bulkhead D radially braced with 4 B.A. rods; compression counterbracing members omitted from all panels.

In this set of experiments the compressive counterbracing members in all panels were omitted, so that, apart from the D bulkhead bracing, there were no redundancies in the framework. The two load systems are shown in the diagram as Nos. 9 and 10, and Table VII. gives the stresses obtained for the two cases. The theoretical stress distribution which would be obtained with a rigid bulkhead, or alternatively for a special arrangement of the external load, had already been calculated *, and the figures reduced to correspond to the altered net shear force are quoted in Table VII. for comparison with the experimental values.

TABLE VII.

Member.	Loads.		
	Theoretical.	No. 9.	No. 10.
C_1D_1	0	0	0
B_1C_1	78	78·4	73·6
A_1B_1	156	154·0	142·2
C_2D_2	−39	−39·2	−36·8
B_2C_2	−1·5	−1·0	0·3
A_2B_2	36	39·6	41·4
C_3D_3	−76·5	−76·0	−71·4
B_3C_3	−105·0	−104·0	−87·9
A_3B_3	−133·5	−133·7	−111·1
C_4D_4	−96	−102·2	−121·6
B_4C_4	−192	−195·4	−227·2
A_4B_4	−283	−294·2	−330·6
C_1D_2	50·5	51·0	47·8
B_1C_2	50·5	49·2	44·6
A_1B_2	50·5	50·0	47·0
C_2D_3	99·5	98·8	92·8
B_2C_3	99·5	102·8	100·4
A_2B_3	99·5	99·2	98·8
C_3D_4	62·5	66·4	79·0
B_3C_4	62·5	60·6	68·6
A_3B_4	62·5	64·4	67·2

* Aeronautical Research Committee R. & M. 971, Table I.

It will be noticed that the stresses in the three cases o this set are in reasonably good agreement in spite of the redundancies being confined to the loaded bulkhead. The tube was insufficiently long to allow definite conclusions to be drawn as to the applicability of the Principle of Saint-Venant to this case, but comparing the results obtained with those of Set No. 1, where all the redundancies were in the panel bracing, it is evident that redundant bracing when in the plane of the bulkhead is far more efficient than when placed in the panels, in conducing to an equalization of stresses.

These two conditions of the framework would appear to bear some analogy to the cases of a solid rod and a thin tube respectively, and it might be a matter of some interest and importance to investigate such cases to determine the distances required for strain equalization.

Conclusion.

The experiments lead to the following general conclusions :—

1. The Principle of Saint-Venant can be applied to the case of a redundant framework.

2. The operation of the principle is very slow if planes parallel to the loading plane are unbraced, even when the framework exhibits a high degree of redundancy in other planes.

3. If the plane of loading is braced, the tendency towards the equalization of strains is pronounced, and the distance required for the variation of strains to become negligible is dependent to a marked extent upon the efficiency of the bracing in this, and parallel planes.

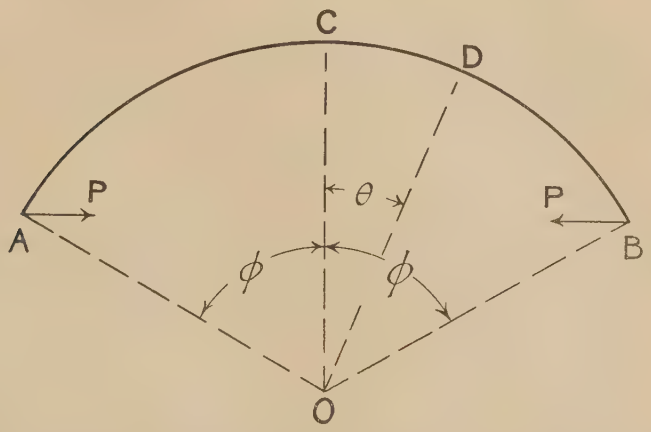
XVI. *On the Effect of Curved Members upon the Elastic Properties of a Framework. By* Professor A. J. Sutton Pippard, *M.B.E., D.Sc., University College, Cardiff* *.

THE elastic properties of a braced framework will govern the amount of its deformation under the action of external loads and also, in the case of a redundant frame, the distribution of internal stresses. Calculations of nodal displacements and stress analysis require, therefore, the introduction of this factor, and this may be conveniently done by the application of strain-energy methods †.

* Communicated by the Author.

† Cp. Phil. Mag. vol. xlv. p. 194 (Jan. 1923).

In general, the component bars of a framework are straight, but in some cases, *e. g.*, in mediæval roof trusses, curved members occur, and these affect the elastic properties of the frame, and consequently its stiffness and stress distribution, to a considerable degree.



The present note indicates a general method for determining the effect of such members and for reducing frameworks containing them to cases in which standard methods of analysis may be used. The case of members curved to a circular arc is alone considered: this is the shape commonly found, but the method is readily adaptable to any other curve.

Let A and B be two nodes of a framework connected by a circular arc of radius R, and subtending an angle 2ϕ at the centre. If the frame is pin-jointed, any force transmitted between A and B must act along the line AB. Let P be such a force.

Then if Δ is the amount by which the distance AB is shortened under the action of P,

$$\Delta = \frac{dU}{dP}, \quad \ldots\ldots \quad (1)$$

where U is the strain-energy of the bar.

If I is the moment of inertia of the cross-section of the bar,

A is the cross-sectional area of the bar ;

E is the modulus of elasticity of the material ;

N is the modulus of rigidity of the material.

Then at any point D on the arc where $\angle COD = \theta$ the resultant actions are :

an axial compression $= P\cos\theta$;

a radial shear $= P\sin\theta$;

a bending moment $= PR(\cos\theta - \cos\phi)$;

and the total strain-energy of the bar is

$$U = \frac{P^2R}{AE}\int_0^{\phi}\cos^2\theta\,.\,d\theta + \frac{P^2R^3}{EI}\int_0^{\phi}(\cos\theta-\cos\phi)^2\,.\,d\theta + \frac{P^2R}{AN}\int_0^{\phi}\sin^2\theta\,.\,d\theta, \quad . \quad . \quad (2)$$

where the first and second terms are the components due to axial load and bending respectively, and the third term is an approximation to the unimportant component due to shear.

Differentiating and evaluating, and giving N the value $\frac{2}{5}E$, we obtain

$$\Delta = \frac{PR}{AE}\left[\frac{7\phi}{2} - \frac{3\sin 2\phi}{4} + \frac{R^2}{k^2}\left(2\phi - \frac{3\sin 2\phi}{2} + \phi\cos 2\phi\right)\right], \quad . \quad . \quad . \quad (3)$$

where k is the radius of gyration of the cross-section.

If the curved bar were replaced by a straight member of the same cross-sectional dimensions, but with such a value of E that Δ remained the same, the elastic properties of the frame would be unaltered.

Let E′ be the modulus of elasticity of such a member. Then, under the action of P, its alteration in length would be $\frac{2PR\sin\phi}{AE'}$, and for this to be equal to Δ we must have

$$E' = E\left[\frac{2\sin\phi}{\frac{7\phi}{2} - \frac{3\sin 2\phi}{4} + \frac{R^2}{k^2}\left(2\phi - \frac{3\sin 2\phi}{2} + \phi\cos 2\phi\right)}\right]. \quad . \quad . \quad . \quad (4)$$

Any framework containing curved members can thus be simplified by replacing all such members by straight bars of the same cross-sections as the originals, but with modified values of E as given by equation (4). Such a simplified frame will be elastically equivalent to the original, and the usual methods for calculating deflexions and stresses can be employed.

The formula of equation (4) was verified by cutting two circular arc members from steel plate and experimentally

obtaining their load-compression curves. These curves were linear up to the yield-point, and the slopes gave the values of E′. The value of E for the material was found experimentally in the usual way. The results of the tests are given in the following table :—

Experiment.	Radius of arc.		Thickness.	2ϕ.	E.	E′/E.		
	Internal.	External.				Experimental.	Calculated.	Error.
No.	inch.	inch.	inch.	degrees.	lb./sq. in.			%
1	4·984	5·982	·727	180	26,960,000	·00346	·00348	0·58
2	4·984	5·982	·727	120	26,960,000	·0164	·0171	4·1

These results show satisfactory confirmation of equation (4). Experimental difficulties in No. 2 which were absent in No. 1 account for the higher percentage error.

The method outlined in this note has been applied to the analysis of stresses in certain roof trusses, including the Westminster Hall roof, for the Building Research Station of the Department of Scientific and Industrial Research, the results being contained in a paper to be published shortly *.

XVII. *Dimensional Analysis viewed from the Standpoint of the Theory of Similitudes.* *By* Mrs. T. Ehrenfest-Afanassjewa, *Leiden (Holland)* †.

THERE seems to be very little lacking at present toward freeing so-called "dimensional analysis" ‡ from all the mysticism which still clings to it, in spite of the great interest many physicists take in it. In this respect I am

* "The Determination of Primary Stresses in Roof Trusses, with special reference to the case of curved members," by A. J. S. Pippard and W. H. Glanville.

† Communicated by Prof. Dr. P. Ehrenfest.

‡ This quite practical designation is given by P. W. Bridgman in his book 'Dimensional Analysis,' New Haven, Yale University Press, 1922. In it are discussed many typical examples of the customary use of dimensional analysis; the difficulties which arrest attempts to give dimensional analysis a theoretical basis also are given prominence in the introduction. As I see it, soundness will not be attained unless the standpoint of the theory of similitudes is assumed basically.

encouraged especially by the work of Campbell *, in which dimensional analysis is intrinsically nothing less than rejected, and is replaced by what I call the theory of similitude †. The necessity of keeping these two methods well separated I pointed out many years ago ‡. Indeed, in his introduction Campbell quotes my paper, but he does not express his agreement with my conception. However, I hope by means of the following analysis to further the desired agreement. Yet the note here presented is not a mere review of my earlier ones, but it embodies deeper insight into dimensional and similitude analysis in two respects: first, concerning the rôle of constants of integration §, and second, concerning the view upon similitude-transformations of different quantities having the same dimension ‖. In addition to this, the difference of opinion between Lord Rayleigh and Riabouchinsky ¶ will also be cleared up.

§ 1. All the views of dimensional analysis are based on the supposition that a physical equation, in which all variable quantities are explicitly given, must be "homogeneous" (that is, having only "dimensionless" coefficients,—such as remain invariant in any change of units consistent with the C.G.S. system).

This supposition really is without foundation, and can immediately be refuted by means of examples **.

Let us examine together the following three equations :—

$$f = -kr, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$f = k\frac{m}{r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$f = k\frac{s}{r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

* Norman Campbell, "Dimensional Analysis," Phil. Mag. xlvii. p. 481 (1924).

† Referred to in German as "Modelltheorie" or "Aehnlichkeits theorie."

‡ T. Ehrenfest-Afanassjewa, "Der Dimensionsbegriff und der Bauphysikal. Gleichungen," *Math. Ann.* lxxvii. p. 259 (1915). On Mr. R. C. Tolman's "Principle of Similitude," Phys. Rev. viii. p. 1 (1916). Also two papers in the Journ. of the Russian Phys.-Chem. Society, 1911.

§ *Cf.* § 5 of this paper.

‖ *Cf.* §§ 7 and 8 of this paper.

¶ D. Riabouchinsky, "The Principle of Similitude," Nature, xcv. p. 591 (1915),

** Compare my previous articles: "Ueber die Willkür bei der Dimensionierung physikalischer Groessen," *Mathem. naturw. Blaetter*, Leipzig, 1905, and *Math. Ann.* lxxvii. p. 259, § 11 (1915).

If we interpret equation (*a*) as the elastic oscillation equation, (*b*) as the Newtonian gravitation equation, and (*c*) as the "angle equation" (relationship between the central angle *f*, length of arc *s*, and radius *r*), *k* will appear in all three equations as a coefficient which depends on the choice of units.

Of course, an advocate of dimensional analysis would immediately find a reason for giving dimensions to the coefficient *k* in equation (*a*) : *k* is not simply a coefficient but a "physical constant" ; that is, a variable quantity, which differs from one material to the next.

But how about equation (*b*)? Perhaps here, too, one would want to furnish an excuse : granted that we find in the entire real world only one kind of gravitating material, and that therefore *k* is a "universal constant" (in contrast to the various kinds of rubber which exert force according to equation (*a*)), there are other *conceivable* worlds in which *k* (with the same choice of units for all the other quantities) would have another numerical value.

But we still have equation (*c*) ; it is clear that in it the coefficient *k* has the dimension of an angle. And yet here neither of the two arguments presented above is valid, and it is therefore impossible to establish the thesis : "in an equation in which all physical quantities are explicitly given the coefficients are dimensionless."

What else is meant by the expression : "there are other conceivable worlds"? Let us compare in this respect examples (*b*) and (*c*) : we may indeed think of worlds in which the relation between the central angle, radius, and length of arc of a circle is in general different from that in our world *, but we cannot conceive of another Euclidean world —*a world in which equation (c) holds*,—in which *k* would have another numerical value ; our intuition tells us directly that this is impossible. Our intuition relative to gravitational force, on the contrary, is very incomplete ; we may write on paper a gravitation equation with a different coefficient *k*, and there is nothing to tell us whether such a formula still has any physical meaning. Thus the pretence

* Thus, for instance, in a world in which the Riemannian geometry were valid, eq. (*c*) would be replaced by the following :

$$\phi = k \frac{s}{\sin \frac{r}{a}},$$

where *a* is the radius of curvature of the space, and *r* the radius of the circle.

that the gravitational constant is not a "coefficient" but a "variable quantity" remains undisputed. But when we have taken account of example (*c*), this pretence will no longer serve for establishing the presumed homogeneity of all physical equations. If nature can allow one non-homogeneous relationship between distinct quantities, as exists in eq. (*c*), what will give us a guarantee that there is not an abundance of other quantities which are also related to each other in non-homogeneous equations? *

If therefore we know nothing else about an equation between certain variables, $x_1\, x_2, \ldots x_m$ except that it exists and that it involves no variables other than these, there exists the possibility that if all these variables were given in it explicitly, it might still involve dimensional coefficients (and that it could not be brought to a homogeneous form by any transformations). In this case, one would obtain a spurious form for it according to the method of dimensional analysis †.

§ 2. Nevertheless, there is the question, whether dimensional analysis may not after all be used with success in cases where we have definite grounds for assuming that the equation sought is certainly homogeneous. To this it is necessary to reply with two remarks: first, that these grounds may still be found illusory; second, that it is easy in the application of dimensional analysis to introduce ambiguities in the solution, which—as we shall see—may be diminished if the "theory of similitudes" is used instead of dimensional analysis The former is so related to the latter in its method of calculating as to be mistaken for it frequently; however, it rests upon other, quite definite

* And, if we do not want to enter uncontrollable discussions about other conceivable worlds, but look upon all coefficients which keep their values unchanged (as far as we are able to judge) as universal constants, an example occurs immediately in the gravitational equation. Presumably Planck's constant h, too, will figure in such a non-homogeneous, still unknown, fundamental equation.

† One might perhaps be inclined to desire a system, other than the C.G.S. system of dimensions, in which all coefficients of all physical equations were indeed dimensionless (the gravitation equation for instance becomes homogeneous, if one chooses a dimension-system—in adaptation to the same equation—so that mass involves the dimension $[L^3T^{-2}]$). But eq. (*c*) directly offers an example of equations which cannot be made homogeneous by any change in the system of dimensions. Besides, it is clear that in general if the number of dimensional universal constants were to be more than two, the problem would already be over-determinate, for each "removal of dimensions" from a coefficient means a decrease in the number of fundamental variables (*i. e.*, of variables whose units may be changed with entire freedom).

principles of pure mathematics, and can yield other results. Above all, its application is independent of the possibility that the equation sought may have dimensional coefficients. To be sure, it requires more data than dimensional analysis, but this is quite natural for a method which often gives more definite results, and never erroneous ones.

Method of Similitudes.

§ 3. The method of similitudes starts with "*fundamental equations*," of which the desired equation is a consequence.

Let us asssume that we know the complete system of fundamental equations of a problem :

$$\left.\begin{aligned} f_1(x_1\ x_2, \ldots x_n) &= 0, \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \\ f_k(x_1\ x_2, \ldots x_n) &= 0. \end{aligned}\right\} \quad \ldots\ldots \quad (1)$$

We will assume that this system "permits certain transformations." That is, if we introduce instead of the quantities $x_1, x_2 \ldots x_n$ other quantities according to certain "*equations of transformation*" :

$$\left.\begin{aligned} x_1 &= \phi_1(x_1', x_2', \ldots x_n'), \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \\ x_n &= \phi_n(x_1', x_2', \ldots x_n'), \end{aligned}\right\} \quad \ldots\ldots \quad (2)$$

we shall have exactly the same equations in the new variables :

$$\left.\begin{aligned} f_1(x_1', x_2', \ldots x_n') &= 0, \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \\ f_k(x_1', x_2', \ldots x_n') &= 0. \end{aligned}\right\}$$

Obviously, every derived equation will also be invariant in undergoing transformations according to (2).

Suppose we look for a relation

$$\Phi(x_1, x_2, \ldots x_m) = 0 \quad \ldots\ldots \quad (3)$$

between a group of variables $x_1, x_2 \ldots x_m)$, $m \leqq n$, which may be a consequence of equations (1). Suppose we succeed in setting up the most general form of invariant relations between the variables $x_1, \ldots x$. Then equation (3), if in general it exists, will obviously appear as a special case of this most general form.

Now a given system of equations (1) may admit, in

general, various kinds of transformations *. We shall choose as "trial-transformations" for our purpose those for which the most general form of relations remaining invariant, as mentioned above, is especially easy to set up.

One such convenient kind of transformations constitutes the "similitude transformations" †. They are represented by

$$\left.\begin{aligned} x_1 &= \xi_1 x_1', \\ x_2 &= \xi_2 x_2', \\ &\cdots \\ x_n &= \xi_n x_n', \end{aligned}\right\} \quad \cdots\cdots \quad (2^*)$$

where $\xi_1, \xi_2, \ldots \xi_n$ are any fixed numbers (transition-factors).

It is clear that no equation between $x_1, x_2, \ldots x_n$ will permit this transformation if each number ξ_i is chosen quite independent of the others ; since the fundamental equations remain invariant, there must exist certain relations of the transition-factors :

$$\left.\begin{aligned} \xi_{r+1} &= \psi_1(\xi_1, \ldots \xi_r), \\ \xi_{r+2} &= \psi_2(\xi_1, \ldots \xi_r), \\ &\cdots \\ \xi_{r+l} &= \psi_l(\xi_1, \ldots \xi_r), \end{aligned}\right\} \quad \cdots\cdots \quad r+l=n \quad (3)$$

* For instance, the system of equations

$$\frac{x^2}{z} + y^2 z = \sin y^2 z,$$

$$ax^2 = \frac{b}{y^2},$$

admits the transformations

$$x = -x', \quad y = -y', \quad z = -z',$$

but also the transformations

$$x = \xi x', \quad y = \eta y', \quad z = \zeta z',$$

where the positive constants ξ, η, ζ, are governed by the equations

$$\frac{\xi^2}{\zeta} = 1, \quad \eta^2 \zeta = 1.$$

The equation $\sin ax = b$ admits the transformation

$$x = \frac{2\pi}{a} + x'.$$

† This designation is not to be taken literally, for in such transformations a geometric similitude is not always produced. Compare remark (*a*) in example 2, § 9.

which we will call "*conditional equations.*" It may be shown, which we will not do here *, but which is readily seen in each concrete example, that these conditional equations may always be put in the form:

$$\left.\begin{aligned} \frac{\xi_{r+1}}{\xi_1^{\alpha_{11}}\,\xi_2^{\alpha_{12}}\cdots\xi_r^{\alpha_{1r}}} &= 1, \\ \cdots\cdots\cdots & \\ \frac{\xi_{r+l}}{\xi_1^{\alpha_{l1}}\,\xi_2^{\alpha_{l2}}\cdots\xi_r^{\alpha_{lr}}} &= 1. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (3^*)$$

The r numbers, $\xi_1, \xi_2 \ldots \xi_r$, may be chosen quite arbitrarily.

The size of the number r and the values of the exponents $\alpha_{11}, \ldots \alpha_{lr}$ depend upon the form of the fundamental equations.

It may be shown further, which again we will not do †, that the most general form of an equation which permits the transformation (2*) with the conditional equations (3*) is as follows:—

$$\mathrm{F}\left(\frac{x_{r+1}}{x_1^{\alpha_{11}}\cdots x_r^{\alpha_{1r}}}, \cdots \frac{x_{r+l}}{x_1^{\alpha_{l1}}\cdots x_r^{\alpha_{lr}}}\right) = 0. \quad . \quad . \quad (4^*)$$

F is any arbitrary function. The number of arguments is that of the conditional equations, so that we get a greater indeterminateness for the equation sought, when more conditional equations connect the transition-factors ξ_i. But it may occur that even in spite of a large number of conditional equations we may obtain in this way a far-reaching determinateness for the equation sought; namely, when the equation sought consists not of all the variables $x_1, x_2, \ldots x_n$, but of a sub-group of them, say $x_1, x_2 \ldots x_m (m < n)$; it may be that among the transition-factors *of these variables alone* there is only a single conditional equation:

$$\frac{\xi_m}{\xi_1^{\alpha_1}\,\xi_2^{\alpha_2}\cdots\xi_{m-1}^{\alpha_{m-1}}} = 1‡.$$

* A proof may be found worked out, for instance, in the work of A. Federmann, "Some general methods of integration of part. diff. equ. of the first order," Iswestia, St. Petersb. Polyt. Inst. xvi. p. 97 (1911).

† *Cf.* my paper in *Math. Ann.* l. c.

‡ *I. e.*, in case a derived equation exists between only $x_1, x_2, \ldots x_m$, it permits freely all the transformations (2*); but then there must be conditional equations among the transition-factors $\xi_1, \xi_2, \ldots \xi_m$ alone (otherwise these factors would be *severally* unrelated, and the equation sought could not remain invariant in every similitude-transformation consistent with (3*)). Therefore these conditional equations may be derived from eq. (3*) by elimination of the other $n-m$ transition-factors. Their number in general is less than l, and may also be 1.

The most general equation of the variables $x_1, x_2, \ldots x_m$ alone will then involve an arbitrary function of a single argument, $\frac{x_m}{x_1^{\alpha_1} x_2^{\alpha_2} \ldots x_{m-1}^{\alpha_{m-1}}}$:

$$F\left(\frac{x_m}{x_1^{\alpha_1} x_2^{\alpha_2} \ldots x_{m-1}^{\alpha_{m-1}}}\right) = 0,$$

which means that we must have

$$\frac{x_m}{x_1^{\alpha_1} x_2^{\alpha_2} \ldots x_{m-1}^{\alpha_{m-1}}} = C,$$

where the only indeterminate is the value of the constant C.

§ 4. Since problems are often treated in physics in which differential equations appear among the fundamental equations, the following comments, too, are necessary :—

1. In case one of the variables represents a differential quotient among other variables, then the system of equations must be extended by an equation which expresses this relationship, for instance :

$$x_1 = \frac{\partial^3 x_2}{\partial x_3 \, \partial x_4^2}.$$

This imposes a conditional equation on the transition-factors, which is easy to find. If we make in our example the transformations

$$x_1 = \xi_1 x_1' \; ; \quad x_2 = \xi_2 x_2' \; ; \quad x_3 = \xi_3 x_3' \; ; \quad x_4 = \xi_4 x_4',$$

and substitute the new variables, we shall have

$$\xi_1 x_1' = \frac{\partial^3 (\xi_2 x_2')}{\partial (\xi_3 x_3') \partial (\xi_4 x_4')^2} = \frac{\xi_2}{\xi_3 \xi_4^2} \frac{\partial^3 x_2'}{\partial x_3' \, \partial x_4'^2}.$$

Since

$$x_1' = \frac{\partial^3 x_2'}{\partial x_3' \, \partial x_4'^2}$$

we must have

$$\xi_1 = \frac{\xi_2}{\xi_3 \xi_4^2}.$$

2. If in the equation sought there appear besides the variables $x_1, x_2, \ldots x_m$, their particular values $x_{01}, x_{02}, \ldots x_{0m}$ (which is always the case when it is an integral of the given

differential equation) *, then one must also note the transformations

$$x_{01} = \xi_{01} x_{01}' ; \quad x_{02} = \xi_{02} x_{02}', \quad . \quad . \quad . \quad (2^{**})$$

where the transition-factors clearly are bound in the conditional equations

$$\frac{\xi_{01}}{\xi_1} = 1 ; \quad \frac{\xi_{02}}{\xi_2} = 1. \quad . \quad . \quad . \quad . \quad (3^{**})$$

§ 5. In connexion with the last comment, we may conveniently formulate the question which I previously touched only slightly †. If differential equations are included among the fundamental equations, and the equation sought is an integral of these, it will always involve particular values of the variables appearing in it, for by means of these the constants of integration may always be evaluated.

We shall therefore always have to consider more than one conditional equation ; beside the (possibly) single equation of the type

$$\frac{\xi_{r+1}}{\xi_1^{\alpha_1} \xi_2^{\alpha_2} \dots \xi_r^{\alpha_r}} = 1$$

there will also be equations of the type

$$\frac{\xi_{i0}}{\xi_i} = 1.$$

Our method will therefore always render an indeterminate solution, of the type ‡

$$\mathrm{F}\left(\frac{x_{r+1}}{x_1^{\alpha_1} x_2^{\alpha_2} \dots x_r^{\alpha_r}}, \frac{x_{10}}{x_1}, \frac{x_{20}}{x_2}, \dots \right) = 0.$$

There arises the question : since most of the fundamental

* Example : in the equation

$$s = s_0 \sin 2\pi \frac{t - t_0}{\mathrm{T}},$$

s_0 is a particular value of s_1 corresponding to $t = t_0 + \pi/4$; t_0 a particular value of t, corresponding to $s = 0$; T a particular value of t, corresponding to the value of t required by the equation

$$\sin 2\pi \frac{t - t_0}{\mathrm{T}} = \sin 2\pi \frac{-t_0}{\mathrm{T}}.$$

† Conf. my article, *Math. Ann.* l. c. § 5; "Bemerk. I." and § 14 "Behaupt. 8."

‡ Thus, for instance, the equation $\frac{dy}{dx} = a$, where a represents a constant of the equation, does not have the solution $\frac{y}{ax} = \text{const.}$ which would be obtained if the particular values of x and y were forgotten

equations with which we deal in physics are differential equations, what value, in general, does the similitude-method have?

The answer is this: the derived equations in which we are interested often are not integrals of the fundamental differential equations, but relationships between only particular values of the variables and the constants of the fundamental equations †. In such cases the similitude method can readily give definite results, for then the transition-factors of the *variables* may be eliminated from the conditional equations, so that finally there is obtained a single conditional equation of only those transition-factors in which we are interested.

§ 6. In the application of the similitude-method it is important to observe the following:—

The number of independent arguments in equation (4*) is equal to the number of conditional equations between the transition-factors under consideration. The latter may be erroneously decreased by overlooking one or another of the fundamental equations of the problem (or, as was mentioned in the preceding section, by forgetting the interdependence of the particular values of the variables). In this way there may be projected an *illusory definiteness* of solution ‡. On the other hand, an *illusory indefiniteness* may occur, if one combines the transition-factors in conditional equations taken from points of view other than those called for by the similitude-method §.

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and only one conditional equation $\frac{\eta}{\alpha\xi}$ were taken into account (where η, ξ, α represent the transition-factors of the transformation $y=\eta y'$, $x=\xi x'$, $a=\alpha a'$), but another: $y=ax+C$, which corresponds to the form $F(y/ax,\ y_0/y,\ x_0/x)=0$, for C may always be chosen so that one obtains either $y-y_0=a(x-x_0)$ or $y=ax$, or $y=ax+\frac{y_0^2}{x_0}$ etc., which all are consistent with the form $F=0$. Besides, this form is still more general than the form $y=ax+C$, for the latter does not involve $y=C\,.\,ax$, where C′ is arbitrary; this, however, is a special case of $F=0$ But this is permissible, for the most general solution of a given differential equation need not be the most general equation which permits the transformation corresponding to the differential equation.

† The simplest examples: (1) the period of oscillation of a gravity pendulum = function of its length, and the acceleration of gravity. (2) Kepler's equation.

‡ This is the case in the example analysed by Einstein. Footnote of the final paragraph.

§ Thus the equating, for example, of the transition-factors of all lengths, if it does not follow directly from the fundamental equations, must be considered as simply *superstitious*. Compare example 2, § 9.

In order to avoid error in the application of the similitude-method, and to obtain the greatest possible definiteness of solution, the two following rules must be observed :—

I. *All* the fundamental equations have to be considered, of which the one desired is an analytical consequence.

II. No conditional equations may be introduced, except those which are imposed on the transition-factors by the fundamental equations of the problem.

Both of these rules are violated in principle in the application of dimensional analysis.

Dimensional Analysis.

§ 7. Dimensional analysis teaches that the form of the equations sought is to be fixed likewise on the basis of "similitude-transformations." Its solution, too, has the form of equation (4*), only the conditional equations—therefore the number r ofindependent transition-factors and the exponents α_{ik}—are not developed from the fundamental equations of the given problem, but :

1. The number of independent transition-factors is fixed once for all ; *i. e.*, they are the transition-factors of the three quantities : length, time, mass.

2. For fixing the exponents α_{ik} those equations are quoted which served historically for introducing the various quantities and fixing their units, and by which the "dimension" † of each quantity is fixed.

We have as a consequence : (1) in cases where the fundamental equations of the problem have dimensional coefficients, the qualifying equations of dimensional analysis are in contradiction with those of the similitude-method ; (2) in cases where all the coefficients of the fundamental equations are dimensionless, there is of course no contradiction, but the number of conditional equations may be larger than is necessary according to the similitude-method ‡.

† *I. e.*, a convention relative to the change of units of related quantities in dependence on the change in units of length, time, and mass. The appearance of such quantities as consequently have zero dimensions cannot be controlled according to dimensional analysis.

‡ That one may in spite of this often obtain the same conditional equations according to both methods results from this, that in general we are not excluded from obtaining the same results by elimination in two different systems of equations (conditional equations of dimensional analysis and those of the similitude-method). *Cf.* Ex. 1, § 9.

The number of unnecessary equations is further enlarged in dimensional analysis, in that the transition-factors of all quantities of the same sort are equated *. Obviously the form of the equation sought does not depend on whether we designate some of its variables as physical quantities of the same kind or of the same dimensions. Hence the equating of the transition-factors of two different quantities (designated in the fundamental equations with different letters!) must be recognized as altogether a violation of rule II.†

§ 8. The last consideration may readily serve for a complete analysis of the difficulty which Mr. D. Riabouchinsky ‡ brought up in his familiar note relative to the method of Lord Rayleigh.

Lord Rayleigh availed himself of dimensional analysis, but used as independent transition-factors not three, but four: those of length, time, heat quantity, and temperature. His investigations yielded for a certain desired equation an arbitrary function of two definite arguments, which may be written:

$$h = ka\theta \mathrm{F}\left(\frac{acv}{k}\right),$$

and which may also be written

$$\Psi\left(\frac{h}{ka\theta}, \frac{acv}{k}\right) = 0.$$

Riabouchinsky thereupon showed that a greater indeterminateness would be obtained if one were to use dimensional analysis in the customary manner, with only three independent transition-factors, dealing with temperature as a "derived quantity" with the dimensions of kinetic energy. There would thus be an additional conditional equation, and consequently an additional argument in the indefinite function of the equation:

$$h = ka\theta \mathrm{F}\left(\frac{v}{ka^2}, ca^3\right).$$

But this is an example of the violation of rule II.: the equation by which temperature is defined as the average kinetic energy of the molecules is not one of the fundamental equations of the problem; it relates temperature with

* *Cf.* remark (*a*) in example 2 in § 9.

† In cases where in spite of this the results of the two methods are the same, it is because the ignoring of fundamental equations (lessening the number of conditional equations) and the equating of transition-factors of quantities of the same kind (increasing the number of conditional equations) compensate each other. *Cf.* Ex. 1, § 9.

‡ D. Riabouchinsky, "The Principle of Similitude," Nature, xcv. p. 591 (1915).

quantities (molecular velocity and molecular mass) which do not occur in any of the fundamental equations of the problem, and *there exists no justification for equating the transition-factors of these quantities to the transition-factors of those quantities of the same kind which actually occur in the fundamental equations.*

Besides it must be observed that if the method of Lord Rayleigh leads to good results, it is because (without his control) the actual fundamental equations of his problem involved no dimensional coefficients.

Illustrations.

§ 9. The examples presented below are most trite, and yet they offer enough material for illustrating all the features of the two theories that we have discussed.

Example 1.—To derive the relation between the time of oscillation T of a simple pendulum, its length l, and the acceleration of gravity, g.

It is assumed that such a relationship exists. The steps taken according to the method of dimensional analysis may be formulated as follows in terms of the similitude-method :—

1. Consider the equation

$$g = \frac{d^2r}{dt^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (*)$$

where r is the distance of the pendulum from the centre of the earth. The transition-factors of the transformations

$$g = \gamma g' ; \quad r = \rho r' ; \quad t = \tau t'$$

are united—in order to leave the equation (*) invariant—in the conditional equation :

$$\gamma = \frac{\rho}{\tau^2}.$$

2. Because of the like nature of the physical quantities l and r the transition-factors λ ($l = \lambda l'$) and ρ are equated :

$$\lambda = \rho.$$

3. The transition-factor τ_0 ($T = \tau_0 T'$) is set equal to τ :

$$\tau_0 = \tau,$$

since T is a particular value of t.

4. The oscillation equation

$$\frac{d^2s}{dt^2} + \frac{g}{l}s = 0, \quad . \quad . \quad . \quad . \quad . \quad (**)$$

of which the desired equation is a consequence, is ignored (!).

Thus is obtained, after elimination of τ and ρ, the conditional equation

$$\frac{\tau_0}{\lambda^{\frac{1}{2}}\gamma^{-\frac{1}{2}}} = 1,$$

whence it follows that

$$T = c\sqrt{\frac{l}{g}}.$$

Thus steps 1 and 2 are a violation of rule II. and "step" 4 is a violation of rule I. Step 2 causes no indeterminateness because the transition-factor ρ is finally eliminated. Steps 1 and 4 compensate each other, because equations (*) and (**) fortuitously yield after the elimination of ρ and τ the same conditional equation, which is possible because—without having previously controlled it—equation (**) is homogeneous.

According to the similitude-method, the following steps would be made:—

1. Consider equation (**) and derive from it the conditional equation *

$$\frac{\sigma}{\tau^2} = \frac{\gamma}{\lambda}\sigma.$$

2. Equate the transition-factors τ and τ_0:

$$\frac{\tau}{\tau_0} = 1.$$

From this one will obtain after elimination of τ the qualifying equation between just those transition-factors under consideration:

$$\frac{\tau_0}{\lambda^{\frac{1}{2}}\gamma^{-\frac{1}{2}}} = 1;$$

therefore

$$T = C\sqrt{\frac{l}{g}}.$$

This result depends only on how the quantities t, g, and l appear in the oscillation equation (**), and it would be the same even if g did not represent an acceleration, but a quantity of any kind you please †.

Example 2.—To formulate the dependence of the time of oscillation of the pendulum on its length l, its distance r from the centre of the planet, and the attracting mass m of the planet.

* The transition-factor σ thus drops out, which shows that on the basis of the similitude-method the form of the derived equations involving s cannot be fixed.

† *Cf.* footnote to example 2.

Dimensional analysis cannot attack this problem at all, because the transition-factors of the quantities considered according to its method are quite independent of each other: in consequence of ignoring the fundamental equations of the problem it furnishes—erroneously—too few (namely, zero!) conditional equations.

According to the similitude-theory the following steps are prescribed:—

1. Consider the fundamental equations:

$$\frac{d^2s}{dt^2} + \frac{g}{l}s = 0; \quad g = k\frac{m}{r^2}, \quad . \quad . \quad . \quad . \quad (A)$$

whence it follows:

$$\frac{1}{\tau^2} = \frac{\gamma}{\lambda}; \quad \gamma = \frac{\mu}{\rho^2}, \quad . \quad . \quad . \quad . \quad (B)$$

where μ and ρ are the transition-factors of the transformations $m = \mu m'$ and $r = \rho r'$, respectively.

2. Put

$$\tau_0 = \tau. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B')$$

In the equation sought the quantities t and g are not to appear; we must therefore see whether they may be eliminated from (B) and (B'). They may; and thus we obtain in consequence a single conditional equation:

$$\frac{\tau_0}{\lambda^{\frac{1}{2}}\rho\mu^{-\frac{1}{2}}} = 1,$$

whence it follows that

$$\mathrm{T} = \mathrm{C}r\sqrt{\frac{l}{m}}.$$

Remarks.—(*a*) Equating the transition-factors ρ and λ—in violation of rule II.—would create an additional conditional equation of the transition-factors under consideration, $\frac{\rho}{\lambda} = 1$, and would cause an illusory indeterminateness, for then we should have the equation

$$\mathrm{F}\left(\frac{\mathrm{T}}{r^{\frac{1}{2}}m^{-\frac{1}{2}}}, \frac{r}{l}\right) = 0,$$

which would permit the form

$$\mathrm{T} = \mathrm{C}r\sqrt{\frac{l}{m}}$$

as well as

$$\mathrm{T} = \mathrm{C}l\sqrt{\frac{r}{m}} \quad \text{and} \quad \mathrm{T} = \mathrm{C}_1\sqrt{\frac{l^3}{m}} + \mathrm{C}_2\sqrt{\frac{r^3}{m}},$$

and as many others as you please.

(*b*) With the aid of the similitude-method we can investigate *selectively* the part played in the equation sought by

just those quantities which interest us, without caring about the others; *i. e.*, we may apply those similitude-transformations in which all the other quantities are unchanged. Thus, for example, we may obtain the following relationship of T, l, and m only (by putting $\rho=1$):

$$\frac{\tau_0}{\lambda^{\frac{1}{2}}\mu^{-\frac{1}{2}}}=1;$$

$$\text{therefore} \qquad T=C\sqrt{\frac{l}{m}}\,*,$$

in which c remains constant only while $\frac{k}{r^2}$ remains constant.

If we want to know how the gravitational constant k affects the time of oscillation, we have to introduce the transformation equation $k=\kappa k'$ among the others (which is independent of whether or not k is a universal constant), and we then obtain:

$$\frac{\tau_0}{\rho\lambda^{\frac{1}{2}}\mu^{-\frac{1}{2}}\kappa^{-\frac{1}{2}}}=1;$$

$$\text{therefore} \qquad T=Cr\sqrt{\frac{l}{km}}.$$

Conclusion.

§ 10. According to this comparison of dimensional analysis with the similitude-method, we see that only the latter yields results essentially dependable, even though often not very definite. However, if the fundamental equations of the problem are unknown, of the two methods there remains only dimensional analysis. It must never be forgotten that in such cases one advances only gropingly, and without experimental or theoretical proof from another quarter one can never be completely certain of the results. Dimensional analysis combined with proof of this kind may be viewed as a systematic method for determining whether in the given problem new and unknown fundamental equations take part which are non-homogeneous relative to the quantities considered; *i. e.* which involve dimensional coefficients or new variables †.

Leiden, Aug. 30, 1925.

* We see that here the quantity m is in exactly the same position as the quantity g in example 1, although it has a different dimension! And that is because it is in the same position in the fundamental equation of this example, as g in that of example 1.

† A pretty example of such an application of dimensional analysis is found in the paper of A. Einstein; *cf.* "Zum gegenwörtigen Stand des Strahlungsproblems," *Phys. Zschr.* x. § 6, p. 189 (1909).

XVIII. *The Roots of Hypergeometric Functions with a numerator and four denominators. By* H. E. H. Wrinch, *M.I.Mech.E., and* D. M. Wrinch, *M.A., D.Sc.**

DURING the last few years, the Generalized Hypergeometric Function has become of increasing importance in applied mathematics. This paper contains certain tables of the roots of certain generalized hypergeometric functions which have important applications in the theory of the vibrations of bars of various cross-sections. Attention was called to the fundamental significance in problems of morphology of the periods of vibration of bars of varying density with cross-sections of various types by Dendy and Nicholson † in 1917.

In the present paper we give roots of the equation

$$\mathrm{F}(\alpha\,;\ \alpha_1,\ \alpha_2,\ \alpha_3,\ \alpha_4,\ ;\ -4(x/4)^4) = 0$$

—for a large range of values of the parameters $(\alpha, \alpha_1, \alpha_2, \alpha_3, \alpha_4)$ —where F is the generalized hypergeometric function with one numerator and four denominators,

$$\mathrm{F}(\alpha\,;\ \alpha_1,\ \alpha_2,\ \alpha_3,\ \alpha_4\,;\ -4(x/4)^4)$$
$$\equiv 1 - \frac{4(1+\alpha)(x/4)^4}{1!\,(1+\alpha_1)(1+\alpha_2)(1+\alpha_3)(1+\alpha_4)}$$
$$+ \frac{4^2(1+\alpha)(2+\alpha)(x/4)^8}{2!\,(1+\alpha_1)(2+\alpha_1)(1+\alpha_2)(2+\alpha_2)(1+\alpha_3)(2+\alpha_3)(1+\alpha_4)(2+\alpha_4)}.$$

These roots are required for an investigation ‡ which develops the general idea put forward by Dendy and Nicholson in the paper already cited and by Dendy in a number of other publications §.

The full discussion of the roots of the equation would require the consideration of the various values taken by the five separate parameters. Such a discussion is not required for the applications under contemplation, though it could be carried out on similar lines.

The special values of the parameters to be included in the

* Communicated by the Authors.

† Proc. Roy. Soc. A, vol. xciii.; Proc. Roy. Soc. B, vol. lxxxix.

‡ Wrinch, Phil. Mag. vol. xlvi. (1923).

§ See, for example, Dendy's Presidential Address to the Quekett Microscopical Club, Journ. Q. M. C. series 2, vol. xiii. (1917). *Cp.* also Nicholson, "The Lateral Vibrations of Sharply-pointed Bars," Proc. Roy. Soc. A, vol. cxvii. (1921).

present discussion are specified as follows : —

Let

$$\alpha_1,\ \alpha_2,\ \alpha_3,\ \alpha_4 = \frac{7s}{4}-2,\ \frac{3s}{2}-2,\ \frac{5s}{4}-2,\ 3s-4\ ;$$

$$\alpha = 3s-\frac{9}{2}*.$$

TABLE I.—$s = 1$.

No. of Root.	x.
1	1·571
2	4·712
3	7·854
4	10·996
5	14·137
6	17·279
7	20·420
8	23·562
9	26·704

TABLE II.—$s = 20/19$.

No. of Root.	x.
1	1·891
2	4·987
3	8·118
4	11·255
5	14·394
6	17·534
7	20·675
8	23·816
9	26·956

TABLE III.—$s = 20/18$.

No. of Root.	x.
1	2·213
2	5·283
3	8·407
4	11·541
5	14·678
6	17·816
7	20·956
8	24·096
9	27·236

TABLE IV.—$s = 20/17$.

No. of Root.	x.
1	2·544
2	5·606
3	8·725
4	11·856
5	14·992
6	18·129
7	21 268
8	24·408
9	27·548

TABLE V.—$s = 20/16$.

No. of Root.	x.
1	2·894
2	5·958
3	9·076
4	12·206
5	15·341
6	18·478
7	21·617
8	24·756
9	27·896

TABLE VI.—$s = 20/15$

No. of Root.	x.
1	3·270
2	6·347
3	9·468
4	12·598
5	15·734
6	18·871
7	22·009
8	25·149
9	28·289

* The quantity s has special significance in the application in question in connexion with the shape of the vibrating rod. See Wrinch, *loc. cit.* p. 275.

TABLE VII.—$s = 20/14$.

No. of Root.	x.
1	3·682
2	6·781
3	9·907
4	13·040
5	16·177
6	19·315
7	22·455
8	25·594
9	28·735

TABLE VIII.—$s = 20/13$.

No. of Root.	x.
1	4·142
2	7·269
3	10·405
4	13·543
5	16·683
6	19·823
7	22·964
8	26·105
9	29·246

TABLE IX.—$s = 20/12$.

No. of Root.	x.
1	4·665
2	7·826
3	10·975
4	14 121
5	17·266
6	20·409
7	23·553
8	26·695
9	29·838

TABLE X.—$s = 20/11$.

No. of Root.	x.
1	5·270
2	8·469
3	11·637
4	14·794
5	17·946
6	21·094
7	24·241
8	27·387
9	30·531

TABLE XI.—$s = 2$.

No. of Root.	x.
1	5·985
2	9·226
3	12·417
4	15·589
5	18·750
6	21 906
7	25·058
8	28·208
9	31·356

Then, we give a number of roots of the equation when s has the values

$s = 20/20,\ 20/19,\ 20/18,\ 20/17,\ 20/16,\ 20/15,$
$20/14,\ 20/13,\ 20/12,\ 20/11,\ 20/10$

intermediate between $s=1$ and $s=2$. The roots are found

obtained by means of the asymptotic expansion for the hypergeometric function obtained by one of the present writers * in 1923.

Note.—We are indebted to the Government Grant Committee of the Royal Society for a grant in aid of the computations contained in this paper.

XIX. *The Field of a Thick Spherical Shell on Einstein's Theory of Relativity.* *By* J. T. Combridge, *M.A.*, *M.Sc.* (*Imperial College of Science*) †.

THE only problem to which Einstein's gravitational equations for the field in attracting matter appear to have been applied is that of a sphere containing a perfect fluid. Opinion is divided as to what restrictions on the components of the "material-energy-tensor" are necessary for the definition of a perfect fluid, but these restrictions are always imposed and the components (pressures and density) specified before a solution of the gravitational equations is attempted ‡. It is, however, possible to extract a great deal of useful information with fewer restrictions. We shall here confine ourselves to a heterogeneous shell such that the layers of equal density are concentric spheres.

From considerations of spherical symmetry we assume that with spherical polar coordinates with their origin at the centre of the shell the quadratic form may be taken as

$$ds^2 = -e^{\lambda}\,dr^2 - r^2\,d\theta^2 - r^2\sin^2\theta\,d\phi^2 + e^{\nu}\,dx_4^2, \quad . \quad (1)$$

where λ and ν are functions of r only, and $x_4 = ct$, c being the velocity of light *in vacuo* in the absence of gravitation. Similarly we assume for the components $T^{\alpha\beta}$ of the material-energy-tensor

$$\left.\begin{array}{l} T^{\alpha\beta} \text{ functions of } r \text{ only, and} \\ T^{\alpha\beta} = 0 \text{ unless } \alpha = \beta. \end{array}\right\} \quad . \quad . \quad . \quad (2)$$

T^{11}, T^{22}, T^{33} are pressures, and T^{44} is the density referred to the coordinates in use. All are zero except at points occupied by matter. The mixed components T^{β}_{α} are given by

$$T^{\beta}_{\alpha} = g_{\alpha\gamma}\,T^{\beta\gamma}$$

* Phil. Mag. vol. xlv. (1923).

† Communicated by Prof. G. B. Jeffery, M.A., D.Sc.

‡ *Cf.* de Donder, 'La Gravifique einsteinienne,' p. 54; Eddington, 'Mathematical Theory of Relativity' (2nd ed.).

and their divergence must vanish—that is, the four conditions

$$(T^{\beta}_{\alpha})_{\beta}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

must be satisfied. The two for which $\alpha=3$ or 4 are satisfied in virtue of (2); the other two give

$$\frac{dT^1_1}{dr}+\frac{1}{r}(2T^1_1-T^2_2-T^3_3)+\frac{1}{2}\frac{d\nu}{dr}(T^1_1-T^4_4)=0, \quad . \quad (4)$$

$$T^2_2=T^3_3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Hence in the case of Newtonian mechanics (ν a constant) the four conditions (3) reduce to the single condition

$$2r\,T^2_2=\frac{d}{dr}(r^2\,T^1_1),$$

which is the usual relation between the radial (T^1_1) and transverse (T^2_2) tensions acting on an element of a thin spherical shell under radial forces *.

The gravitational equations to be satisfied are

$$G_{\alpha\beta}=-2\kappa(T_{\alpha\beta}-\tfrac{1}{2}g_{\alpha\beta}\,T), \quad . \quad . \quad . \quad . \quad (6)$$

where

$$T_{\alpha\beta}=g_{\beta\gamma}T^{\gamma}_{\alpha}; \quad T=g_{\alpha\beta}T^{\alpha\beta}=T^{\alpha}_{\alpha}.$$

κ is a constant factor which for a weak gravitational field is equal to $4\pi/c^2$ times the constant of gravitation. With the quadratic form (1), $G_{\alpha\beta}\equiv 0$ unless $\alpha=\beta$, while the "four identities" known to connect the contracted covariant derivatives of the $G_{\alpha\beta}$ yield nothing that is not already contained in (3).

We thus obtain three independent equations, namely :

$$\frac{1}{2}\ddot{\nu}-\frac{1}{4}\dot{\lambda}\dot{\nu}+\frac{1}{4}\dot{\nu}^2-\frac{1}{r}\dot{\lambda} \quad = \quad \kappa(T^1_1-2T^2_2-T^4_4)e^{\lambda}, \quad . \quad (7)$$

$$\frac{1}{r}(\dot{\nu}-\dot{\lambda})+\frac{2}{r^2}(1-e^{\lambda})=-2\kappa(T^1_1 \qquad +T^4_4)e^{\lambda}, \quad . \quad (8)$$

$$-\frac{1}{2}\ddot{\nu}+\frac{1}{4}\dot{\lambda}\dot{\nu}-\frac{1}{4}\dot{\nu}^2-\frac{1}{r}\dot{\nu} \quad = \quad \kappa(T^1_1+2T^2_2-T^4_4)e^{\lambda}, \quad . \quad (9)$$

where we have used (5) and dots denote differentiation with respect to r. If these three equations be solved for T^1_1, T^2_2 and T^4_4 and the values substituted in equation (4) we find that the latter is satisfied, so that it represents no

* See, for example, Prescott's 'Applied Elasticity,' p. 327.

new condition. Instead of (7), (8), and (9) above, we use (7) + (8) + (9) and (7) + (9), together with equation (4). The first of these gives

$$-\frac{2}{r}\dot{\lambda}+\frac{2}{r^2}(1-e^{\lambda})=-4\kappa e^{\lambda}T_4^4,$$

whence

$$e^{\lambda}=\left\{1-\frac{2}{r}m(r)\right\}^{-1}, \quad . \quad . \quad . \quad . \quad (10)$$

where

$$m(r)\equiv\kappa\int_0^r T_4^4 r^2\,dr. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The second gives

$$-\frac{1}{r}(\dot{\lambda}+\dot{\nu})=2\kappa(T_1^1-T_4^4)e^{\lambda},$$

whence

$$\lambda+\nu=2\kappa\int_0^r re^{\lambda}(T_4^4-T_1^1)\,dr,$$

and so

$$e^{\nu}=\left\{1-\frac{2}{r}m(r)\right\}e^{\int_0^r F(r)\,dr} \quad . \quad . \quad . \quad (12)$$

with

$$F(r)\equiv 2\kappa r\left\{1-\frac{2}{r}m(r)\right\}^{-1}(T_4^4-T_1^1) \quad . \quad . \quad . \quad (13)$$

If it is desired to specify further the nature of the material composing the shell, the corresponding relation between T_1^1, T_2^2 and T_4^4 may be laid down. From this T_2^2 may be eliminated since it is given explicitly by (4), leaving a relation between T_1^1 and T_4^4. If in addition the density-component T_4^4 be given as a function of r, the problem is completely determinate. What is, however, of greater interest is the conclusion to be derived from the above results regarding the field in the interior of the shell.

Let a and b be the radii of the bounding surfaces of the shell ($b > a$). Then for $a \geqq r \geqq 0$, $T_a^8=0$ and so $m(r)$ and $F(r)$ are both zero. Hence in the cavity of the shell e^{λ} and e^{ν} are both constants and space-time is Euclidean. This is a particular case of the analogy of the theorem in classical potential-theory that the potential is constant in the cavity of such a shell.

For $r \geqq b$,

$$m(r)=\kappa\int_a^b T_4^4 r^2\,dr\,; \quad \int_0^r F(r)\,dr=\int_a^b F(r)\,dr:$$

since T_1^1 and T_4^4 are zero except for values of r between a and b. But these being definite integrals are both constants. Denote the former by M and the latter by k. Then

$$e^{\lambda} = \left(1 - \frac{2M}{r}\right)^{-1} \quad \text{and} \quad e^{\nu} = e^{k}\left(1 - \frac{2M}{r}\right).$$

Comparing these values with those of the usual solution for the field of the sun, we see that the constant of integration M in that solution is really $\kappa \int_0^R T_4^4 r^2 dr$, where R is the sun's radius *. The establishment in this manner of the identity of the constant of integration with the inertial mass is believed to be new. It does not require, as Schwarzschild's work does, the assumption that T_4^4 is constant throughout the sphere. Identity with the gravitational mass follows as usual from the equations of motion.

For $b \geqq r \geqq a$, the expressions for $m(r)$ and $F(r)$ exist only between the limits a and b, and so the "potentials" over any spherical surface of radius r, concentric with the origin and lying in the material, are those due to a spherical shell whose inner and outer radii are a and r respectively, the matter outside the surface again contributing nothing to the field. The analogy with a classical theorem is once more obvious.

XX. *On the Absolute Value of Entropy.* *By* Meghnad Saha, *D.Sc., Professor of Physics, Allahabad University, and* Ramankanta Sur, *M.Sc., Government Intermediate College, Allahabad* †.

ACCORDING to Boltzmann, the entropy of a thermodynamical system is represented by the equation

$$S = k \log_e W. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

S = entropy, k = Boltzmann's gas-constant, W = probability of the state.

There are different ways of calculating the probability W for different thermodynamical systems. In previous years, W was used in a relative sense, in terms of some standard state. By W was meant the mathematical probability,

* If e^{ν} is to be unity when r is infinite, k must be zero.

† Communicated by the Authors.

hence it was always a fraction. Moreover, it remained indeterminate to the extent of an additive constant.

To Planck we owe the conception of the "Thermodynamical probability." This is proportional to the mathematical probability, but not quite equal to it. The mathematical probability is a fraction, while the thermodynamical probability is a whole number. Planck has developed methods for calculating the thermodynamical probability of different systems—*e.g.*, a perfect gas and black body radiation. As is well known, this idea led, in the hands of its author, to the development of the Quantum theory, which is now responsible for progress along all lines in physical science.

There are, however, a few points which are not yet clear. Some of these refer to the fundamental assumptions of the theory, others refer to the mode of application of the fundamental ideas. The exact nature of these obscure points can only be made clear by reference to the actual working, which we now proceed to do.

§ 1. *Theory of Perfect Gases**.

Let us take a large number N of molecules enclosed within a volume V in the gas-kinetic sense. To calculate the probability of the system, the volume is divided into a number of cells denoted by 1, 2, 3, ... n, containing N_1, N_2, N_3 .... N_n molecules respectively. The thermodynamical probability is defined as the total number of complexions (*i. e.*, the total number of ways in which this distribution can be effected). It is easy to see that

$$W_n = \frac{N!}{N_1!\, N_2! \ldots . N_n!} \quad . \quad . \quad . \quad . \quad (2)$$

The mathematical probability

$$W_{mn} = \frac{W_n}{\Sigma W_n} = W_n \,.\, n^{-N}. \quad . \quad . \quad . \quad (2{\cdot}1)$$

The summation ΣW_n is taken over all positive values of N_1, N_2, etc. consistent with the condition

$$N_1 + N_2 + \ldots . N_n = N.$$

Let $$\frac{N_1}{N} = w_1, \quad \frac{N_2}{N} = w_2 \ldots .$$

* The subject matter of this section is merely an abstract of § 113–§ 134 of Planck's 'Warmestrahlung,' 5th edition.

Then with the help of Stirling's formula, it can be easily shown that

$$\log W_n = -N \sum_{r=1}^{r=n} w_r \log w_r. \quad . \quad . \quad . \quad . \quad (3)$$

The actual or equilibrium value of $\log W_n$ is obtained by making it maximum subject to the prescribed conditions. Let ϵ_r = average energy per molecule in the cell r. Then the total energy

$$E = N_1\epsilon_1 + N_2\epsilon_2 + \ldots . N_n\epsilon_n$$

$$= N\Sigma w_r\epsilon_r = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\Sigma w_r = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From equations (3), (4), (5), we can deduce that in case of equilibrium

$$w_r = \alpha e^{-\beta\epsilon_r}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From the relation $\frac{\partial S}{\partial E} = \frac{1}{T}$ it can be shown that

$$\beta = \frac{1}{kT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From equations (5) and (6)

$$\alpha = \frac{1}{\Sigma e^{-\epsilon_r/kT}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and it can easily be shown that the free energy

$$F = kNT \log \alpha ; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

α, however, remains indeterminate, and it cannot be calculated without the introduction of some further hypothesis.

By an application of Liouville's law, Planck shows that for a system obeying the canonical laws of Hamilton the motion is completely defined if the positional (q) and the momenta (p) coordinates corresponding to each individual degree of freedom of each particle are given. In this case he shows that the phase integral

$$H = \ldots . \iiint \ldots . dq_1 dp_1 dq_2 dp_2 \ldots . dq_f dp_f \quad . \quad (10)$$

(the integral being taken for all the degrees of freedom for a particle), remains unchanged by subsequent events. H is known as the extension of the elementary region of the phase space. According to classical theory, H may have any infinitely small value up to zero, but according to the

quantum theory H has always got a finite, though small, invariant value.

The summation $\Sigma e^{-\frac{\epsilon_n}{kT}}$ can now be effected.

$$\Sigma e^{-\frac{\epsilon_n}{kT}} = \frac{\Sigma e^{-\frac{\epsilon_n}{kT}} dq_1 dp_1 dq_2 dp_2 \ldots . dq_f dp_f}{H}. \quad . \quad (11)$$

For monatomic gases, H must refer to the representative particle in the cell r, having the coordinates x_r, y_r, z_r, and velocity components u_r, v_r, w_r.

Taking $$\epsilon_r = \tfrac{1}{2}m(u_r^2 + v_r^2 + w_r^2) + \epsilon_0, \quad . \quad . \quad . \quad (12)$$

where ϵ_0 denotes the unalterable internal energy of an atom at rest, and

$$dp_1 dp_2 dp_3 = m^3 du_r dv_r dw_r.$$

We obtain

$$\Sigma e^{-\frac{\epsilon_r}{kT}} = \frac{V}{H} e^{-\frac{\epsilon_0}{kT}} (2\pi m k T)^{3/2}. \quad . \quad . \quad . \quad (13)$$

With this value of $\Sigma e^{-\frac{\epsilon_r}{kT}}$, neglecting ϵ_0,

$$S = kN \left\{ \frac{V}{H} (2\pi m k T)^{3/2} \right\} + \tfrac{3}{2} kN. \quad . \quad (14)$$

According to the classical gas laws,

$$S = kN \log \{ V T^{3/2} \} + i, \quad . \quad . \quad . \quad . \quad (14{\cdot}1)$$

where i is independent of T and V, but depends upon N. As far as the calculation of gas laws and specific heat is concerned, the exact value of i is immaterial; but if we wish to study the chemical behaviour of the gas, the vapour pressure, etc., the knowledge of i is essential, as was first pointed out by Nernst in connexion with his Heat Theorem.

Now to show how i depends upon N we take p identical vessels, each of volume V, containing the same quantity of the same gas side by side. Then suppose the sides be made to collapse suddenly and the p volumes are made to mix with each other. No change has been made in the system. The entropy can be calculated by adding the entropies of the p vessels, each of volume V. Thus for the entropy of the whole gas occupying the volume pV we have

$$S = kNp \log (V T^{3/2}) + pi(N), \quad . \quad . \quad . \quad (14{\cdot}2)$$

and this must equal

$$k\overline{Np} \log (\overline{pV} \, . \, T^{3/2}) + i(pN),$$

which is the entropy of a gaseous mass of $p\overline{N}$ particles occupying the volume $p\overline{V}$.

Hence $$pi(\mathrm{N}) = k\mathrm{N}p \log p + i(p\mathrm{N}).$$

The above relation is satisfied if

$$i(\mathrm{N}) = -k\mathrm{N} \log \mathrm{N}.$$

Thus we can deduce from the classical theory that

$$\mathrm{S} = k\mathrm{N} \log \left[\frac{\mathrm{V}}{\mathrm{N}} \mathrm{T}^{3/2} \mathrm{A}\right], \quad . \quad . \quad . \quad . \quad (14{\cdot}3)$$

where A is independent of N, T, and V.

From Planck's theory, we have

$$\mathrm{S} = k\mathrm{N} \log \left[\frac{\mathrm{V}}{\mathrm{H}} (2\pi mk\mathrm{T}e)^{3/2}\right] . \quad . \quad . \quad . \quad (14)$$

Comparing the two expressions, we find that H must vary as N. Planck puts $\mathrm{H} = \mathrm{N}h^3$. But this is, however, not quite clear from the expression for H, for

$$\left.\begin{aligned} \mathrm{H} &= \iiint dq_1 dp_1 dq_2 dp_2 dq_3 dp_3, \\ &= h^3, \end{aligned}\right\} \quad . \quad . \quad . \quad (15)$$

if we put, according to the canons of the quantum theory,

$$\iint dq \,.\, dp = h \text{ (Planck's constant).}$$

Sackur and Tetrode *, who were the first to calculate the value of i, proceeded in a different way. According to Sackur the thermodynamic probability is not equal to our W_n, but it is equal to

$$\frac{\mathrm{W}_n}{\mathrm{N}!} \text{ or } \frac{1}{\mathrm{N}_1! \, \mathrm{N}_2! \ldots . \mathrm{N}_n!}.$$

The value of H, according to Sackur, is

$$\iint dq_1 dp_1 dq_2 dp_2 dq_3 dp_3 = h^3.$$

Tetrode's procedure was identical.

Attention to this point has recently been called by Ehrenfest and Trkal †, who have introduced a new method of dealing with the thermodynamical problems, *e. g.* dissociation equilibrium and vapour pressure, in which all these difficulties are avoided. We shall return to this method shortly. Planck has justified his assumption, viz. $\mathrm{H} = \mathrm{N}h^3$, by taking into account the permutability of the molecules, but the reasoning is rather difficult to follow.

* Sackur, *Ann. d. Physik*, xl. Tetrode, *loc. cit.* xxxix.

† Ehrenfest and Trkal, Proc. Amst. Akad. xxiii. (1920).

§ 2. *Ehrenfest's Method.*

Ehrenfest has introduced a very general method for dealing with the thermodynamical behaviour of different and complex systems, like mixtures of gases reacting with each other. We shall confine our attention to the case of perfect gases.

Ehrenfest replaces the entropy function S by another function $\{\gamma\}$ which is allied but not equal to W. $\{\gamma\}$ is supposed to represent the total phase space described by the system and is defined in the following way :—Let the system consist of N particles. Then each particle describes a sub-phase space $\{\mu\}$, where

$$\{\mu\} = \ldots\ldots\iint\ldots\ldots dq_1 dp_1 dq_2 dp_2 \ldots\ldots dq_f dp_f. \quad . \quad (16)$$

The total $\{\gamma\}$-space described by the system is then given by

$$\{\gamma\} = \mathrm{P}\prod_{\mathrm{N}}\{\mu\}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

the product extending over all the particles. P represents the permutability of the particles.

Now, in our case, *i. e.*, for monatomic gases,

$$\{\gamma\} = \ldots\ldots\iiint\ldots\ldots dx_r dy_r dz_r\, d(mu_r)\,.\,d(mv_r)\,.\,d(mw_r), \quad (17{\cdot}1)$$

$$mu_r = p_{1r}, \quad mv_r = p_{2r}, \quad mw_r = p_{3r}.$$

Now
$$\Sigma p_{1r}^2 + p_{2r}^2 + p_{3r}^2 = 2m\mathrm{E}, \quad . \quad . \quad . \quad (17{\cdot}2)$$

where E = total kinetic energy and m is the mass of a particle.

Hence
$$\{\gamma\} = \frac{\mathrm{V}^{\mathrm{N}}(2\pi m\mathrm{E})^{\frac{3\mathrm{N}}{2}}}{\Gamma\left(\frac{3\mathrm{N}}{2}\right)}. \quad . \quad . \quad . \quad . \quad (18)$$

Putting now
$$\mathrm{E} = \frac{3\mathrm{N}}{2}k\mathrm{T},$$

$$\log\{\gamma\} = \mathrm{N}\log\{\mathrm{V}(2\pi mke\mathrm{T})^{3/2}\}. \quad . \quad . \quad (19)$$

According to Sackur-Tetrode :—

$$\mathrm{S} = k\mathrm{N}\log\left\{e^{5/2}\frac{\mathrm{V}}{\mathrm{N}h^3}(2\pi mk\mathrm{T})^{3/2}\right\}$$
$$= k\log\mathrm{W}.$$

Comparing the two expressions,

$$\mathrm{W} = \frac{\{\gamma\}}{h^{3\mathrm{N}}\,\mathrm{N}!}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

§ 3.

Ehrenfest and Trkal have not traced any connexion between $\{\gamma\}$ and W. But from equations (18), (19), and (20), it is possible not only to connect W and $\{\gamma\}$ for any general system, but also to lay down a general theorem for the calculation of the probability of any system. This we now proceed to do.

According to Planck, the probability W is a whole number. But whenever in physics we wish to determine the absolute value of any quantity, we must as well lay down a "unit" for it. Now let us see what is meant by "Unit Probability."

The idea of "Unit Probability" is intimately connected with the zero of entropy; for $S = k \log W$, and when $W = 1$, $S = 0$. According to the second law of thermodynamics, this takes place when a condensed system is reduced to absolute zero; for a reversible engine acting between this system and another system at a finite temperature T will be able to convert all the heat energy abstracted into mechanical work.

We can suppose this to take place in another way. Suppose we have a gas at a finite temperature. The particles are moving in a chaotic way and at a distance from each other. Suppose all of them suddenly begin to move with identical velocity in the same direction, with the proviso, however, that the total kinetic energy remains the same. Then if this system, on coming into contact with another body and suffering inelastic collision, transfers the whole of its energy to that body, we can say that the heat motion has been completely converted into mechanical work. Thus the idea of absolute zero, and zero of entropy, presupposes a system of particles absolutely devoid of all motion. But this is not sufficient. If the particles which are devoid of all motion remain at a distance from each other, then, owing to mutual attraction and there being no motion, they will begin to move towards each other, and kinetic energy will again be developed and can again be converted into mechanical work. For an attracting system, motion, and with it the energy available from the system, will entirely stop when the particles are packed together in the closest manner possible.

We assume that such a system possesses unit probability. Let the value of γ-space for such a system be denoted by $\{\gamma\}$.

We may remark here that these considerations apply only if we regard the atoms as the final constituents of matter.

This, however, is not the case, and therefore, even when the state pictured above has been reached, the electrons of one atom will react mechanically on the other atoms and electrons; and motion will never be entirely absent. Thus we cannot conceive of an absolute zero of temperature unless we picture to ourselves a state in which the protons and electrons have combined in some unknown way and annihilated all matter. We can therefore talk of absolute zero in a world where there is no matter. But according to the generalized theory of relativity, there can be neither space, time, nor any physical quantity in a world which is entirely devoid of matter. Hence we come to a conclusion which has been previously reached by Nernst, viz., in the phenomenal world it is impossible to reach the absolute zero of temperature.

We shall now proceed to calculate the thermodynamical probability of a system in the terms of $\{\gamma\}_0$ as unity. The probability of the state of a system is proportional to the phase space $\{\gamma\}$ described by the system. Therefore the thermodynamical probability at a finite temperature

$$W = \frac{\{\gamma\}}{\{\gamma\}_0}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

We have now to find out the value of $\{\gamma\}_0$.

Let us suppose that in the system there are N particles, each particle having f degrees of freedom. We shall follow Ehrenfest's considerations in calculating $\{\gamma\}_0$. According to the definition, for a single particle

$$\{\mu\} = \ldots \iint \ldots dq_1 dp_1 dq_2 dp_2 \ldots dq_f dp_f. \quad . \quad (16)$$

Let us suppose that each particle is a Planck-resonator and confine our attention to one degree of freedom only. According to the quantum theory its phase-point (q, p) must lie at $p=0$, $q=0$, or on one of the ellipses h, $2h$, ..., the area between two consecutive ellipses being given by

$$\iint dq\, dp = h\,*.$$

Ehrenfest attaches a "weight" h to each one of these ellipses, and in particular also to the point $(p=0,\ q=0)$. Now, in our case, *i. e.*, for a system at absolute zero, none of the degrees of freedom of any particle is excited : or the phase of every particle for each degree of freedom is at $(p=0,\ q=0)$.

* *Vide* Ehrenfest and Trkal, Proc. Amst. Soc. xxiii. p. 179 (1920).

Hence, for a single particle,

$$\{\mu\} = \ldots\ldots\iint\ldots\ldots dq_1 dp_1 dq_2 dp_2 \ldots\ldots dq_f dp_f$$
$$= h^f.$$

For the whole system

$$\prod_N \{\mu\} = h^{fN}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Again the N particles can be arranged amongst themselves in N ! ways. Combining this with (22), we obtain

$$\{\gamma\}_0 = h^{fN} \underline{N}\,! \quad . \quad . \quad . \quad . \quad . \quad (23)$$

To sum up, the thermodynamic probability in Planck's sense is given by

$$W = \frac{\{\gamma\}}{h^{fN} . \underline{N}} . \quad . \quad . \quad . \quad . \quad . \quad (20{\cdot}1)$$

This will cover all cases.

On the basis of this law we shall now calculate the entropy of a system consisting of diatomic molecules.

§ 4. *Entropy of a Gas consisting of Diatomic Molecules.*

In this case we shall ignore the rotation of molecules about the axis of symmetry and also all internal motions of atoms in the molecule. Therefore, each molecule has only five degrees of freedom, three of these being translational and two rotational.

Thus
$$\{\gamma\}_0 = h^{fN} \underline{N}$$
$$= h^{5N} \underline{N}, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where N denotes the total number of molecules considered.

Now, for a single molecule,

$$\{\mu\} = \int\ldots\ldots dx dy dz d\theta d\psi dp_1 dp_2 dp_3 dp_4 dp_5$$
$$= V . 4\pi . \int\ldots\ldots dp_1 \ldots\ldots dp_5. \quad . \quad . \quad . \quad . \quad (25)$$

Therefore γ-space for the total system is given by

$$\{\gamma\} = \prod_N \{\mu\}$$
$$= V^N . (4\pi)^N . \int\ldots\ldots dp_{1r} dp_{2r} \ldots\ldots dp_{5r} \ldots\ldots, \quad (26)$$

the integrals being taken for all molecules, dp_{1r}, dp_{2r}, etc. denote the momenta of the different molecules.

The total kinetic energy of the molecules being given, the integration is to be taken over all possible values of the

momenta which are consistent with it. If E be the kinetic energy given, we have

$$\Sigma\frac{p_{1r}^2}{2m}+\frac{p_{2r}^2}{2m}+\frac{p_{3r}^2}{2m}+\frac{p_{4r}^2}{2a}+\frac{p_{5r}^2}{2b}=\mathrm{E}, \quad . \quad . \quad (27)$$

where m is the molecular mass and a and b represent the moments of inertia. The molecules being all similar, these quantities (m, a, and b) have the same values for all the molecules. The total number of terms in the left-hand side of equation (27) is 5N.

Hence

$$\{\gamma\}=\mathrm{V}^{\mathrm{N}}.(4\pi)^{\mathrm{N}}.\int\ldots.dp_{1r}\,dp_{2r}\ldots.dp_{5r}\ldots.$$

$$=\mathrm{V}^{\mathrm{N}}.(4\pi)^{\mathrm{N}}.\sqrt{\pi}^{5\mathrm{N}}.\frac{\sqrt{\mathrm{E}^{5\mathrm{N}-1}}}{\left|\left(\frac{5\mathrm{N}}{2}\right)\right.}.\{(2m)^{3/2}.(2a)^{1/2}.(2b)^{1/2}\}^{\mathrm{N}}, \quad . \quad . \quad . \quad (28)$$

since N is very large, we may put $5\mathrm{N}$ for $5\mathrm{N}-1$.

$$\{\gamma\}=\mathrm{V}^{\mathrm{N}}.(4\pi)^{\mathrm{N}}.\frac{\sqrt{2\pi\mathrm{E}^{5\mathrm{N}}}}{\left|\left(\frac{5\mathrm{N}}{2}\right)\right.}.(m^{3/2}.a^{1/2}.b^{1/2})^{\mathrm{N}}$$

$$=\frac{\mathrm{V}^{\mathrm{N}}.(4\pi)^{\mathrm{N}}.\sqrt{2\pi\mathrm{E}^{5\mathrm{N}}}.(m^{3/2}.a^{1/2}.b^{1/2})^{\mathrm{N}}}{\left(\frac{5\mathrm{N}}{2}\right)!}. \quad (28{\cdot}1)$$

Hence

$$\mathrm{W}=\frac{\{\gamma\}}{\{\gamma\}_0}=\frac{\{\gamma\}}{h^{5\mathrm{N}}.\mathrm{N}\,!} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$=\frac{\mathrm{V}^{\mathrm{N}}.(4\pi)^{\mathrm{N}}.\sqrt{2\pi\mathrm{E}^{5\mathrm{N}}}.(m^{3/2}.a^{1/2}.b^{1/2})^{\mathrm{N}}}{h^{5\mathrm{N}}.\mathrm{N}\,!\left(\frac{5\mathrm{N}}{2}\right)!}. \quad (29{\cdot}1)$$

Using Stirling's formula and putting $\mathrm{E}=\frac{5}{2}\mathrm{N}k\mathrm{T}$, we obtain

$$\mathrm{W}=\left\{\frac{e^{7/2}.4\pi\mathrm{V}.(2\pi k\mathrm{T})^{5/2}.m^{3/2}.a^{1/2}.b^{1/2}}{\mathrm{N}.h^5}\right\}^{\mathrm{N}}. \quad (29{\cdot}2)$$

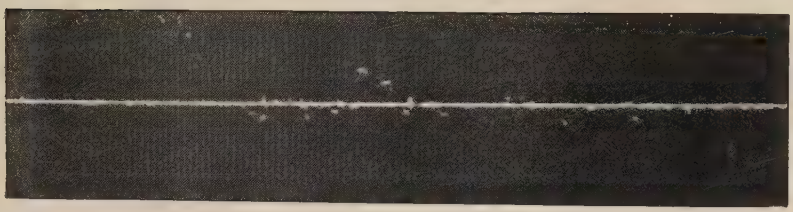
$$\mathrm{S}=k\log\mathrm{W}$$

$$=\mathrm{N}k\log\left\{\frac{e^{1/2}.4\pi\mathrm{V}.m^{3/2}.a^{1/2}.b^{1/2}.(2\pi k\mathrm{T})^{5/2}}{\mathrm{N}.h^5}\right\}. \quad (30)$$

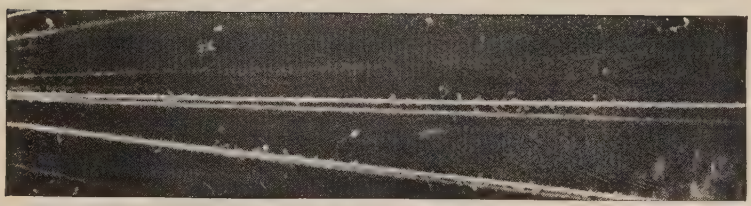
It may be emphasized here that the theorems $\mathrm{E}=\frac{3}{2}\mathrm{N}k\mathrm{T}$ for monatomic gases and $\mathrm{E}=\frac{5}{2}\mathrm{N}k\mathrm{T}$ for diatomic gases have not been assumed here, but followed directly from the theory. The calculations have not been reproduced here.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

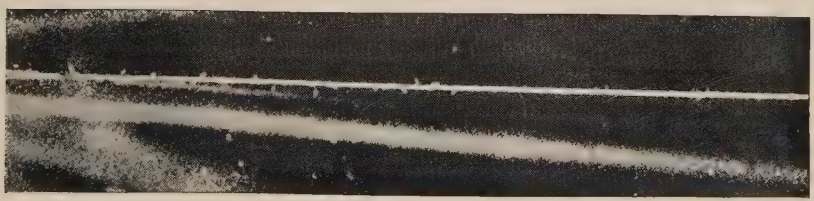
1. Hydrogen. ×3·8



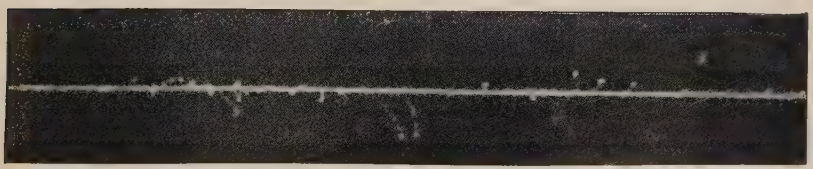
2. Helium. ×2·3



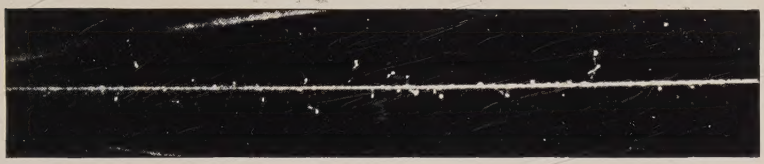
3. Argon. ×3·3



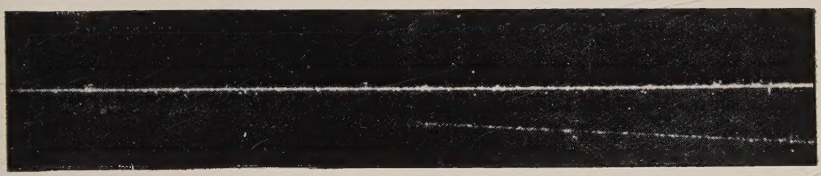
4. Hydrogen. ×4·4



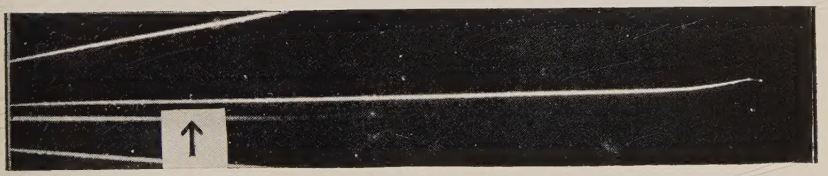
5. Hydrogen. ×3·6



6. Hydrogen. ×3·6



7. Hydrogen. ×2·0



8. Helium. 2·2

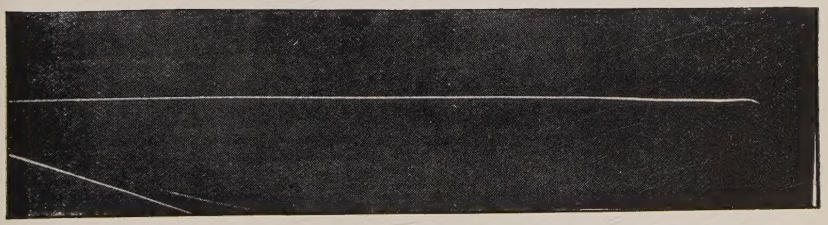


FIG. 2.

FIG. 3.